Journal of Alloys and Compounds 509 (2011) 6004–6008

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Structural, optical and electrical properties of $CuIn_5S_8$ thin films grown by thermal evaporation method

M. Gannouni*, M. Kanzari

Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs -ENIT BP 37, Le belvédère 1002-Tunis, Tunisie

ARTICLE INFO

Article history:
Received 20 June 2010
Received in revised form 6 February 2011
Accepted 7 February 2011
Available online 12 February 2011

Keywords:
$CuIn_5S_8$
Spinel structure
Annealing
Optical properties
Electrical properties

ABSTRACT

Stoichiometric compound of copper indium sulfur ($CuIn_5S_8$) was synthesized by direct reaction of high purity elemental copper, indium and sulfur in an evacuated quartz tube. The phase structure of the synthesized material revealed the cubic spinel structure. The lattice parameter (a) of single crystals was calculated to be 10.667 Å. Thin films of $CuIn_5S_8$ were deposited onto glass substrates under the pressure of 10^{-6} Torr using thermal evaporation technique. $CuIn_5S_8$ thin films were then thermally annealed in air from 100 to 300 °C for 2 h. The effects of thermal annealing on their physico-chemical properties were investigated using X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), scanning electron microscope (SEM), optical transmission and hot probe method. XRD studies of $CuIn_5S_8$ thin films showed that as-deposited films were amorphous in nature and transformed into polycrystalline spinel structure with strong preferred orientation along the (3 1 1) plane after the annealing at 200 °C. The composition is greatly affected by thermal treatment. From the optical transmission and reflection, an important absorption coefficient exceeds 10^4 cm^{-1} was found. As increasing the annealing temperature, the optical energy band gap decreases from 1.83 eV for the as-deposited films to 1.43 eV for the annealed films at 300 °C. It was found that $CuIn_5S_8$ thin film is an n-type semiconductor at 300 °C.

1. Introduction

The ternary semiconductor compounds have a wide range of potential applications in device technology due to the presence of three different chemical components that allow, at least in principle, the tailoring of several important physical properties. The physics of these compounds span many areas of fundamental and technological interest. They have been used as light emitting diodes, non-linear optical devices, photochemical cell applications and photovoltaic solar cells [1].

One of these ternary semiconductors which have attracted considerable attention [2] is the compound $CuIn_5S_8$. Thin films and single crystals of $CuIn_5S_8$ have been deposited by various methods, such as sequential process [3], modified Bridgman method [4], single-source organo-metallic chemical vapour deposition [5] and normal freezing method [6]. In literature, some data about the properties of $CuIn_5S_8$ single crystals have been studied [7–9]. However, only few attempts to produce $CuIn_5S_8$ thin films are known [2,3–10]. Among the reported data, it was mentioned that $CuIn_5S_8$ valency has disordered spinel structure (cubic, Fd3 m) on the tetrahedral sites and can be written by the general formula $(Cu^{+1}In^{+3})_t(In_4{}^{+3})_oS_8{}^{-2}$, where the subscripts *t* and *o* indicate tetrahedral and octahedral sites, respectively [11]. The lattice constant is $a = 10.6736$ Å [12]. $CuIn_5S_8$ is an n-type semiconductor with direct transition [5]. The band gap of $CuIn_5S_8$ is near 1.5 eV [13,14] and the temperature dependence of the band gap showed 1.35 and 1.32 eV at 0 K and 300 K, respectively [4–12]. These values are very close to the theoretical values suggested for obtaining a maximum efficiency in solar cell applications [15,16].

To the best of our knowledge, the properties of $CuIn_5S_8$ thin films have never been studied in detail and the effects of thermal treatment have not been reported yet. In this work, we report the synthesis of $CuIn_5S_8$ thin films on glass substrates by thermal deposition technique under particular growth conditions, then, we have studied how structural, optical and electrical characteristics of these films change as a function of annealing in the air in the temperature range 100–300 °C.

2. Experimental details

2.1. Synthesis of $CuIn_5S_8$

Stoichiometric amounts of the elements of 99.999% purity Cu, In, and S were used to prepare the initial ingot of $CuIn_5S_8$. The mixture was sealed in vacuum in a quartz tube. In order to avoid explosions due to sulfur vapour pressure, the quartz tube was heated slowly (20 °C/h). A complete homogenization could be obtained by keeping the melt at 1000 °C for about 48 h. The tube was then cooled at rate 7 °C/h. So, the cracking due to thermal expansion of the melt on solidification was avoided. Crushed powder of this ingot was used as raw material for the thermal evaporation.

* Corresponding author. Tel.: +21697587918.
E-mail address: gm_mounir@yahoo.fr (M. Gannouni).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.02.047

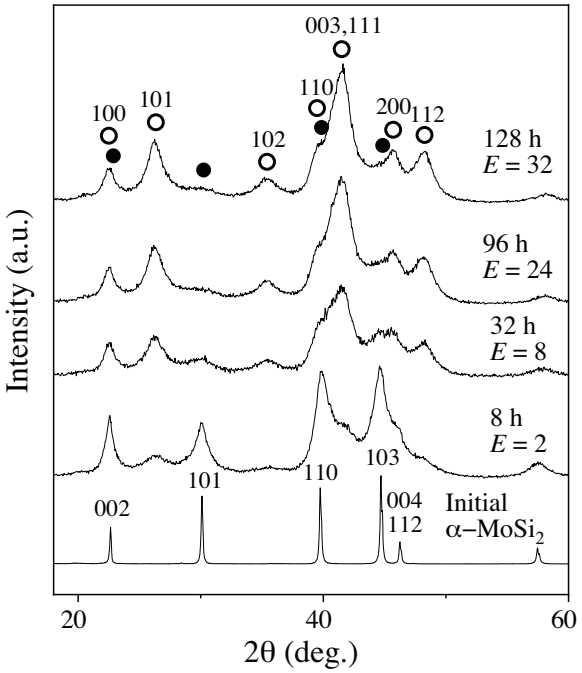

Fig. 1. XRD pattern of $CuIn_5S_8$ powder.

2.2. Film preparation

Evaporated thin films were grown from $CuIn_5S_8$ powder by vacuum evaporation using resistively heated tungsten boats. Thermal evaporation sources were used to be controlled either by the crucible temperature or by the source powder. The pressure during evaporation was maintained at 10^{-6} Torr. Corning 7059 glasses were used as substrates. The film thickness was calculated from the positions of the interference maxima and minima of reflectance spectra using a standard method [17]. The film thickness was found to be ~600 nm. The average deposition rate was around 1 nm s^{-1}. Some of the deposited films were subjected to the post air-annealing procedure in the temperature range 100–300 °C with an increment of 50 °C for 2 h.

2.3. Characterization

The structural properties were determined by the X-ray diffraction technique using CuKα radiation (λ = 1.542 Å). X-ray patterns was carried out to determine the lattice parameter (a), the phases present and the orientation of the synthesized $CuIn_5S_8$ powder and thin films prepared by vacuum deposition method. It is also used for studying the thermal annealing effect on the structure of the as-deposited films. A comparison with JCPDS file cards was done for the establishing the observed peaks. The surface morphology was examined using Philips XL-30 scanning electron microscope (SEM). Optical transmittance and reflectance were measured at normal incidence with an UV–visible-NIR Shimadzu 3100S spectrophotometer in the wavelength range 300–1800 nm at room temperature with the light beam incident on the substrate side with a microglass side as reference. Film resistance was measured between two gold ohmic electrodes previously deposited by thermal evaporation. The type of conductivity of these films was determined by the hot probe method.

3. Results and discussion

3.1. Structural and compositional analysis

3.1.1. Structural of $CuIn_5S_8$ powder

In Fig. 1, XRD pattern of the source powder indicates that it has a single phase of cubic spinel structure and not another phase which exists in the structure. This was verified by JCPDS (Joint Committee on Powder Diffraction Standards) database with card number 24-361 [18]. The main peaks are located at 2θ values of 27.84°, 33.67°, 44.15° and 48.36° with the reflection planes of (3 1 1), (4 0 0), (5 1 1) and (4 4 0) respectively. These reflections in XRD pattern are also in good agreement with the reported values [12]. The Miller indices ($h\,k\,l$), the observed and calculated interplanar spacing (d) and the relative intensities (I/I_0) of the diffraction lines are listed in Table 1. The calculated and observed interplanar spacing are found to be in good agreement with each other. The deduced value of the unit cell parameter for this crystal (a) is found to be 10.667 Å. This value is in good agreement with those reported by several authors [12,19,20]. An examination of the results obtained shows that there are no forbidden reflections ($h\,k\,0$) with $h+k=4n+2$ detected for this compound (check Table 1). The absence of (2 0 0), (4 2 0) and (6 4 0) reflections indicates that there are no "A" site ordering as was observed in analogous chromite spinels [21]. Thus, this crystal can be assigned to the conventional space group Fd3 m [12].

Table 1
X-ray powder diffraction data for $CuIn_5S_8$ crystals (λ_{Cu} = 1.5418 Å).

I/I_0 (%)	Bragg angle 2θ (°)	d_{hkl} (Å) (Calc)	d_{hkl} (Å) (Obs)	($h\,k\,l$)
32	14.514	6.135	6.103	111
29	23.699	3.763	3.754	220
100	27.837	3.203	3.205	311
17	29.082	3.072	3.070	222
51	33.678	2.662	2.661	400
10	36.758	2.442	2.445	331
19	41.515	2.172	2.175	422
44	44.166	2.052	2.051	511
71	48.307	1.882	1.884	440
10	50.677	1.801	1.801	531
12	54.406	1.687	1.686	620
20	56.607	1.628	1.626	533
10	57.288	1.610	1.608	622

3.1.2. Structure of $CuIn_5S_8$ thin films

Fig. 2 shows the results of our XRD measurements for as-deposited and films annealed at 100–300 °C. As seen in the figure, the as-deposited films (Fig. 2a) show amorphous structure in nature. However, under thermal treatment the spectra demonstrate that the films have been always grown with a preferred (3 1 1) orientation according to the angular positions at (2θ = 27.84°) which we have assigned to the cubic $CuIn_5S_8$ spinel phase, this result is in agree with which reported by several authors [5–22]. It is also evident from the figure that two different types of films could be distinguished.

The first one (Fig. 2(b) and (c)), films annealed at 100 and 150 °C showed only one small diffraction peak in the (3 1 1) reflection due to the poor crystallinity of the samples. In the second one, films are annealed at temperatures higher than 200 °C, the films annealed

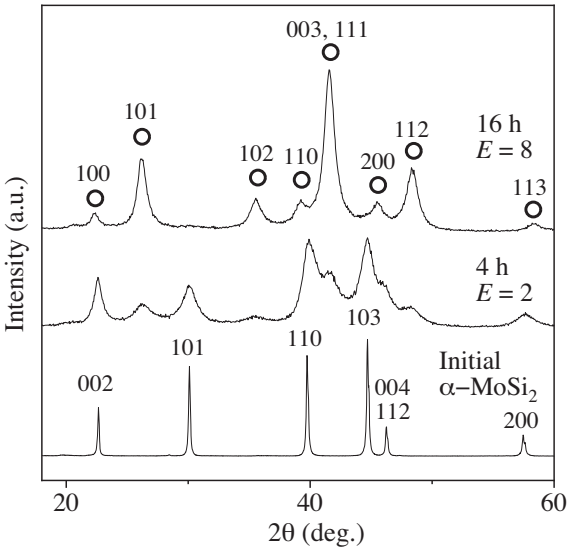

Fig. 2. XRD pattern of as-deposited and thermally annealed $CuIn_5S_8$ thin films.