World Journal of Condensed Matter Physics, 2013, 3, 164-168
Published Online November 2013 (http://www.scirp.org/journal/wjcmp)
http://dx.doi.org/10.4236/wjcmp.2013.34026

Influence of Iodine Pressure on the Growth of $CuIn_{1-x}Ga_xSe_2$ Thin Films Obtained by Close-Spaced Vapor Transport "CSVT"

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Received July 24th, 2013; revised September 6th, 2013; accepted September 21st, 2013

ABSTRACT

We present the results concerning photovoltaic materials $CuIn_{1-x}Ga_xSe_2$ thin films, which were obtained by close-spaced vapor transport "CSVT". The influence of the iodine pressure on the growth of $CuIn_{1-x}Ga_xSe_2$ thin films was studied. The thin films were characterized by Energy Dispersive Spectrometry (EDS), Scanning Electron Microscope (SEM), hot point probe method, X-Ray Diffraction (XRD), Photoluminescence, and Optical response (Photoconductivity). At high pressure, the deposition rate was very important. The films were relatively thick and homogeneous with large grains dimensions. These films are formed of crystals placed in a preferential orientation depending on the plan (112). At low pressure, the films were thin and inhomogeneous with relatively small grains. These films of crystals didn't have preferential orientation.

Keywords: Chemical Vapor Deposition; $CuIn_{1-x}Ga_xSe_2$; Thin Films; Chalcopyrite; Photovoltaic

1. Introduction

Chalcopyrite semiconductors $CuInSe_2$, $CuGaSe_2$ and their solid solution are well known as promising candidates for the fabrication of thin film heterojunctions for photovoltaic application. A conversion efficiency of 20% was reported for solar cells based on $Cu(In,Ga)Se_2$ [1]. Several processes are available for commercial application: Flash Evaporation [2], MOCVD [3], Electrodeposition [4], rf Sputtering [5], Coevaporation [6], Spray Pyrolysis [7], Selenization [8], rapid thermal processing (RTP) [9] or Close-Spaced Vapor Transport "CSVT".

In this paper, we study the influence of the iodine pressure on the growth of $CuIn_{1-x}Ga_xSe_2$ thin films obtained by the "CSVT" method. Energy Dispersive Spectrometry (EDS) and X-ray Diffraction (XRD) were used to calculate the compositions and lattice parameters of the films. Scanning Electron Microscope (SEM) enabled us to check their quality (grains size and morphology). Photoluminescence and photoconductivity allowed us to check their optical properties.

2. Experiment

The "CSVT" method needs a very simple and inexpensive reactor (**Figure 1**) described in [10]. It consists of a vertical quartz tube, with an inner diameter of about 20 mm, and a length of 10 - 20 cm, attached to a vacuum system. At the bottom of this reactor, there was a silice support on which the $CuIn_{1-x}Ga_xSe_2$ source (chip with a thickness e = 1 mm prepared from grains powder < 5 µm under a pressure of 5×10^3 kg/cm^2) [11] is putted. A soda lime glass substrate plate was set above the source at a close distance (0.5 mm < d < 3 mm), by means of a ring spacer of quartz glass. The transport reagent, composed of iodine grains, was located at the upper part of the substrate. The complete system was installed on an external SiC rod. The source temperature depends on the electric voltage applied to this SiC heating element, the quartz plate thickness of ring spacer, and the distance d' between the reactor and the heating element. The substrate temperature is a function of the source temperature, the distance d between the source and the substrate, and the

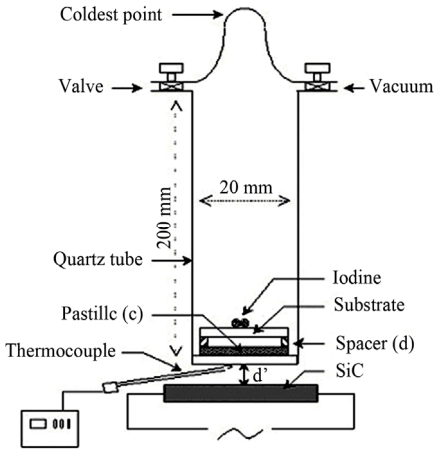

Figure 1. Schematic diagram of the "CSVT" reactor.

gases pressure inside the reactor.

The reaction begins when iodine vaporizes and invades the tube; the pressure of the iodine was determined by the temperature (t_{cp}) of the coldest point in the tube [11], generally at the level of the top.

The iodine vapor pressure (P_{I2}) (**Figure 2**) was calculated from the following equation:

$$\log_{10} P = \left(-0.2185\, A/K\right) + B \qquad (1)$$

where P is the pressure expressed in Torrs, K is the temperature in Kelvin, and A is the molar heat of vaporization in calories per gram mole (A = 13056.6 and B = 9.237273).

Iodine decomposes and reacts with the chip surface by etching. The gaseous elements are transported to the substrate, slightly colder than the source (about 50˚C to 100˚C). These elements settle and reconstitute the material.

3. Results and Discussion

Two series of $CuIn_{1-x}Ga_xSe_2$ ($0 \le x \le 1$) compound thin films corresponding to two values of the iodine pressure were studied. The vapor iodine pressure is varied by varying the temperature (t_{cp}) of the coldest point in the tube (30˚C corresponding to P_{I2} = 0.66 Torrs and 70˚C to 8.31 Torrs) (**Figure 2**). At low iodine pressure (t_{cp} = 30˚C, P_{I2} = 0.66 Torrs), the films obtained are thin (**Table 1**) and inhomogeneous. Two different zones were observed. The first is at the center, formed by melted selenium and crystals. The second, is the area around the center formed by well oriented crystals following a several preferential directions ((112), (220), (204), (316), (116)) indicated by X-ray spectra (**Figure 3(a)**).

At high pressure (P_{I2} = 8.31 Torrs) corresponding to t_{cp} = 70˚C, thick films (**Table 1**) were obtained during a shorter time of transport compared to the low pressure case. These films were homogeneous and formed by well oriented crystals following the direction (112) (**Figure 3(b)**).

In both cases, the size of crystals increases with the proportion of gallium. The lattice parameters a and c vary only linearly with x (**Figure 4**). These values decrease as the gallium concentration increases [12-14], since the gallium atom is much smaller than that of Indium. In all cases, c/a ratio is found to be nearly 2.

The analysis of the chemical composition by EDS (**Figure 5**) shows the presence of a small quantity of

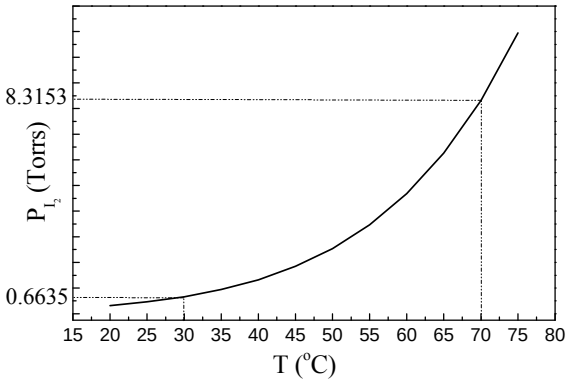

Figure 2. The iodine vapor pressure (P_{I2}) is shown as a function of the temperature. This curve was calculated using Equation (1).

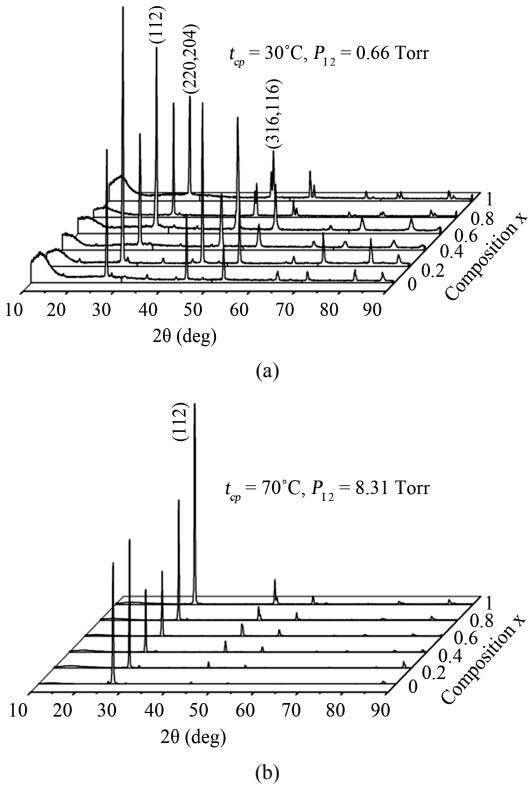

Figure 3. X-ray diffraction patterns of $CuIn_{1-x}Ga_xSe_2$: (a) t_{cp} = 30˚C, P_{I2} = 0.66 Torr; (b) t_{cp} = 70˚C, P_{I2} = 8.31 Torr.

Table 1. Thickness, conductivity type and deposition time of different $CuIn_{1-x}Ga_xSe_2$ samples.

$CuIn_{1-x}Ga_xSe_2$		t_{cp} = 30˚C, P_{I2} = 0.66 Torr			t_{cp} = 70˚C, P_{I2} = 8.31 Torr		
	x	*Time of deposition* (min)	*Thickness* (μm)	*Conductivity type*	*Time of deposition* (min)	*Thickness* (μm)	*Conductivity type*
$CuInSe_2$	0	30	4.2	*p*	20	6.80	*p*
$CuIn_{0.8}Ga_{0.2}Se_2$	0.2	30	6.3	*p*	20	7.50	*p*
$CuIn_{0.6}Ga_{0.4}Se_2$	0.4	30	4.3	*p*	20	9.97	*p*
$CuIn_{0.4}Ga_{0.6}Se_2$	0.6	30	5.4	*p*	20	9.44	*p*
$CuIn_{0.2}Ga_{0.8}Se_2$	0.8	30	13.2	*p*	20	24.2	*p*
$CuInGaSe_2$	1	30	15.6	*p*	20	29.80	*p*

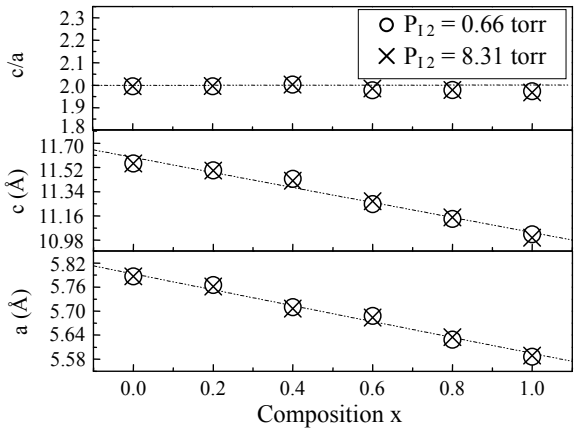

Figure 4. Lattice parameters (a and c) for $CuIn_xGa_{1-x}Se_2$: (○) t_{cp} = 30˚C, P_{I2} = 0.66 Torr and (×) t_{cp} = 70˚C, P_{I2} = 8.31 Torr.

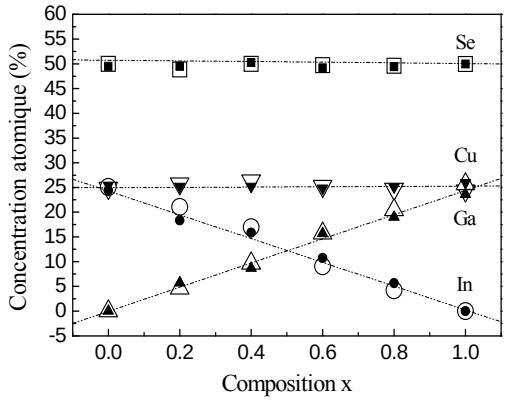

Figure 5. Composition of $CuIn_xGa_{1-x}Se_2$ thin films determined by EDS as a function of the source composition x: ▼Cu, ●In, ▲Ga, ■ Se (t_{cp} = 30˚C, P_{I2} = 0.66 Torr), and ∇ Cu, ○ In, Δ Ga, □ Se (t_{cp} = 70˚C, P_{I2} = 8.31 Torr).

iodine in the films prepared at high P_{I2}, whereas iodine is not detected in those grown at low pressure. Iodine may be removed by annealing at 100˚C. **Figure 6** shows the morphologies of the surface, showing that the sizes of crystals prepared at high P_{I2} are bigger (10 μm < Φ < 25 μm). The crystals have a better orientation than those grown at low P_{I2} (3 μm < Φ < 10 μm). This result shows

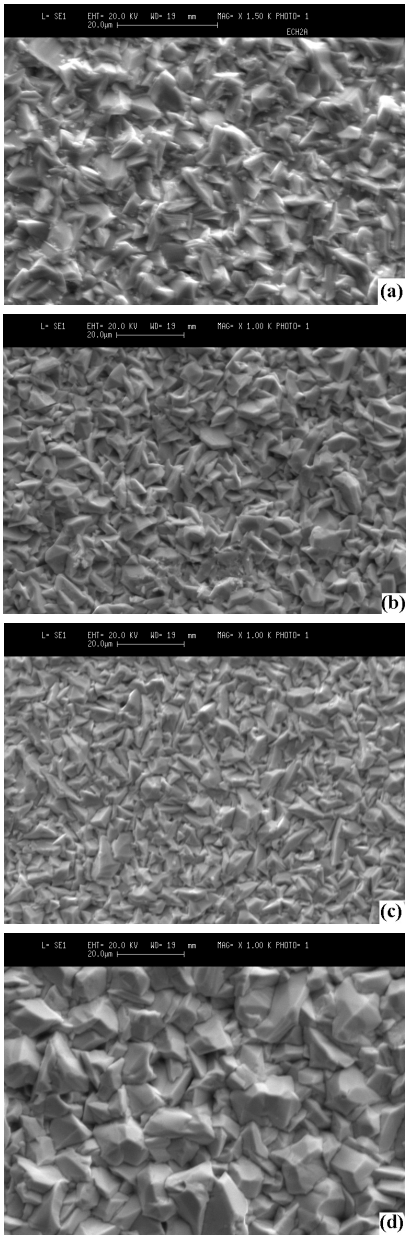

Figure 6. Surfaces SEM micrographs of the films: (a) $CuInSe_2$; (b) $CuGaSe_2$ (t_{cp} = 30˚C, P_{I2} = 0.66 Torr); (c) $CuInSe_2$; (d) $CuGaSe_2$ (t_{cp} = 70˚C, P_{I2} = 8.31 Torr).

that the growth with a high iodine pressure is better.

Figures 7(a) and **(c)** show the spectra of Photoluminescence at liquid Helium temperature (4.2 K) of the alloy $CuIn_{1-x}Ga_xSe_2$ thin films (x = 0 and x = 1) prepared at high P_{I2}. An increase in the gap value of the materials $CuIn_{1-x}Ga_xSe_2$ as a function of the concentration of Ga was observed. The band gap energy value at room temperature is determined in analyzing our compounds by spectral Photoconductivity [15]. **Figures 7(b)** and **(d)** illustrate the spectra of Photoconductivity $((\alpha hv)^2$ as a function of hv) of the $CuIn_{1-x}Ga_xSe_2$ thin films (x = 0 and x = 1) prepared at high P_{I2}. These values are in good agreement with those found by Photoluminescence and in literature [15-17].

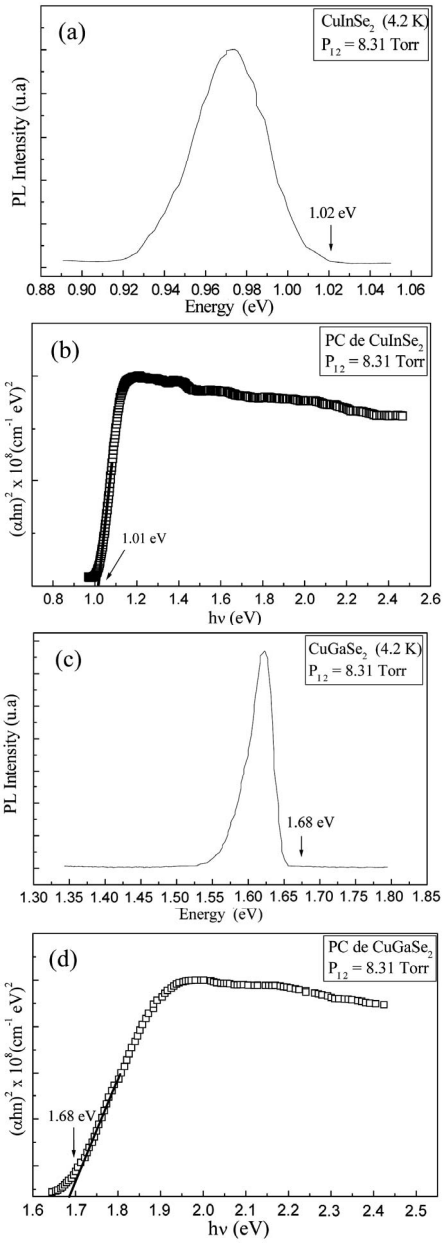

Figure 7. ((a), (c)) Variation of PL dominant peak of $CuIn_{1-x}Ga_xSe_2$ thin films (x = 0 and x = 1) prepared at high P_{I2}; (b, d) The spectra of Photoconductivity $((\alpha hv)^2$ as a function of (hv) of the $CuIn_{1-x}Ga_xSe_2$ thin films (x = 0 and x = 1) prepared at high P_{I2}.

The band gap of the thin films which prepared at low iodine pressure (t_{cp} = 30˚C, P_{I2} = 0.66 Torrs) could not be observed, caused probably by the present of the melted selenium, or the thin films prepared at these low pressure are not brilliant.

4. Conclusion

$CuIn_{1-x}Ga_xSe_2$ thin films at two different iodine pressures were studied. At high pressure, the deposition rate is very important. The films are relatively thick and homogeneous with large grains dimensions. These films are formed of crystals placed in a preferential orientation depending on the plan (112). At low pressure, the films are thin and inhomogeneous with relatively small grains. These films of crystals didn't have preferential orientation. The characterization by Photoluminescence and Photoconductivity allows us to determinate the band gap values of the thin films prepared at high P_{I2} which vary from 1.02 eV to 1.68 eV. The band gap of the thin films prepared at low P_{I2} is not observed, probably due to the present of the melted selenium, or the no brilliant thin films prepared at this low pressure.

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