CuIn_{0.7}Ga_{0.3}Se₂ thin films' properties grown by close-spaced vapor transport technique for second-generation solar cells

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Abstract

In this paper, CuIn_{0.7}Ga_{0.3}Se₂ (CIGS) thin films are deposited on both glass (SLG) and glass/SnO₂:F (SLG/FTO) substrates, by close-spaced vapor transport technique. The Hall effect measurements are performed in the temperature range (300–438 K) for the two SLG/CIGS samples namely CIGS1 and CIGS2, grown at substrate temperature (T_s) of 470 °C and 510 °C, respectively, to investigate the temperature effect on the electrical parameters such as hole concentration (p), conductivity (σ) and mobility (μ). As results, from Arrhenius diagram of (p) and (σ), bandgap energy (E_g) of about 1.38 eV and 1.24 eV are extracted for CIGS1 and CIGS2, respectively. Besides, activation energies (E_a) at 563.9 meV and 239.4 meV are determined for CIGS1 whereas values at 584.2 meV and 72.7 meV are obtained for CIGS2. Furthermore, average mobilities of 1.83 cm²/V s and 1.77 cm²/V s are achieved for CIGS1 and CIGS2 thin films, respectively. Pure aluminum (Al) Schottky contacts are deposited on the front side of FTO/CIGS thin film-devices by physical vapor deposition. Current–voltage (I – V) characteristics are measured and used to extract the electrical parameters of FTO/CIGS/Al Schottky diode using the one diode model. The electrical parameters including series resistance (R_s) of about 93.7 Ω and an ideality factor (n) around 3.47 indicate that the generation–recombination mechanism is predominant.

Keywords CIGS · Thin film · CSVT · Hall effect · Schottky contact

Introduction

The photovoltaic (PV) material Cu–III–VI₂ is currently one of the most promising materials for producing thin-film solar cells. Among them, CuInSe₂ (CIS) with a chalcopyrite structure has been used as an absorber layer in PV devices [1]. It is a direct bandgap semiconductor material and has a large absorption coefficient (10⁵ cm^{−1}) [2]. To produce efficient PV devices it is important to match the bandgap of the absorber layer to the solar spectrum [3]. The ideal E_g for

the solar spectrum is 1.4 eV, however, CIS has only E_g of 1.02 eV. For that, the E_g of CIS can be increased by partial substitution of indium (In) cation with other group III elements such as gallium (Ga). The Ga amount (x) increases the CIGS bandgap from 1.0 eV for CIS ($x=0$) to about 1.68 eV for CuGaSe₂ (CGS) ($x=1$). Until now, the polycrystalline CIGS-based thin films solar cell has reached an efficiency conversion record of about 22.6% [4]. Several methods have been adopted to grow CIGS layers, such as co-evaporation [5], RF-magnetron sputtering [6, 7], electrodeposition [8], multi-layer precursor method [9], rapid thermal processing (RTP) [10]. All these techniques are mainly complex and expensive. In contrast, the close-spaced vapor transport technique (CSVT), using iodine as transport agent offers several advantages among them, simplicity and the possibility to use a large substrate with large surfaces. This method is of less cost since that, the elaboration of CIGS polycrystalline thin films is done without secondary vacuum [11–14].

It is well known that the performance of the devices based on semiconductors and integrated circuits depends on the quality of the metal/semiconductor contacts. Schottky contacts (i.e., rectifier) have been used as test means to

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investigate both the surfaces of the semiconductors material and their physical/electrical properties [15, 16]. Then, to prepare efficient Schottky contacts, good understanding of these properties is crucial. Al/p-CIS Schottky junctions have been fabricated and characterized by several researchers and important results have been obtained. Chan and Shih [17] have investigated the electrical properties of Al/p-CIS structure using current–voltage (I – V) and capacitance–voltage (C – V) measurements. Furthermore, Tecimer et al. [18] have studied the electrical properties of Al/p-CIS/Mo structure and obtained their forward and reverse bias I – V characteristics in a wide temperature range of 100–300 K. Again, Hamrouni et al. [19] have investigated the temperature effects on electrical properties of Al/p-CIS/FTO thin-film Schottky junction using I – V , C – V characteristics and the impedance measurements in the temperature range of 300–425 K. Accordingly, the I – V characteristic at (RT) has confirmed that the junction behaves as a Schottky diode. Also, it has been concluded that, the high value of ideality factor, (3.98) which has obtained from $dV/d \ln(I)$ versus the current density at RT, is probably due to both the potential drop and the recombination through the interfacial layer. Moreover, the C – V measurements have indicated that the carrier concentration of annealed CIS films is about 10^{15} cm^{-3} while both the depletion layer width and the barrier height decrease with T . From the impedance spectra, it has been founded that R_s , R_{sh} , and C decrease with the increase of the annealing temperature.

While considerable research effort has been devoted to the investigation of the CIS-based Schottky diodes, only few studies were reported on the CIGS Schottky structures. Therefore, the present work includes two main parts. First, we have studied the temperature dependence on the electrical parameters of SLG/p-CIGS/Cu structures, which are obtained by depositing copper (Cu) on front side of CIGS

layer by PVD, in the temperature range of 300–428 K using the Hall Effect technique. Second, a Schottky junction has been fabricated by depositing Al on front side of SnO_2 :F/p-CIGS thin film using PVD technique, and (I – V) characteristic has been measured at RT. The electrical parameters of the proposed structure have been extracted using the one-diode model and they have served to understand the predominant current conduction phenomena.

Experimental details

Using our CSVT [11–14], polycrystalline CIGS thin films with a thickness of about $\sim 2 \mu\text{m}$ were deposited on two types of substrates; SLG and SLG/FTO. The principle of the CSVT is based on the achievement of a chemical reversible equilibrium and the transport in a gaseous phase. Its important feature is the close spacing between the source and the substrate which is less than 1 mm, and which leads to a significant change in the transport mechanisms.

After establishing a primary vacuum in the horizontal sealed reactor, Fig. 1, a quartz holed spacer is introduced between the source and the substrate that are arranged face to face and heated separately with two different temperatures, where the difference between them is assumed to be some tens of degrees. The transporting agent, which is the solid iodine in the case of chalcopyrite semiconductors, diluted in a carrier gas which is the inert argon, reacts with the source which is the CIGS powder to form a volatile compound. This latter is then transported to the substrate where the reverse reaction takes place. The thin films are obtained with a polycrystalline structure. Their grain size can be controlled by T_s and iodine pressure in the quartz reactor. This process is done without secondary vacuum [11–14].

Fig. 1 Schematic of horizontal CSVT reactor system

The surface morphology of the layers is studied by scanning electron microscope (SEM) JEOL JSM-7001F. The composition studies are done by energy-dispersive X-ray spectroscopy (EDS) through JEOL JSM 5310 LV equipment. The crystalline phases are examined using X-ray diffraction (XRD) by a Philips PW1729 diffractometer.

Afterwards, Cu-Ohmic and Al-Schottky contacts were deposited through masks onto SLG/CIGS and FTO/CIGS thin films, respectively, by Torr SQM-160 PVD system. Cu and Al of 99.9999% purity were used. Previously and to remove impurities, the CIGS layers were immersed in a mixture of bromine/methanol (0.1/0.9) solution for 30 s, rinsed with deionized water and dried in the furnace at 70 °C for 5 min. The masks were pre-cleaned with ethanol and rinsed with deionized water. Then, they were degreased in a bath of hydrochloric acid (HCl) for 15 min, followed by repeated rinsing with deionized water. This operation is completed by washing the masks with ethanol for 15 min followed by a rinse for 5 min with deionized water and then they were dried in the furnace at 70 °C for 5 min.

In case of Schottky structure, the circular Al-Schottky contacts with a diameter of about 1 mm and a thickness of about 50 nm were thermally evaporated at a pressure of 7.47×10^{-7} kPa. The similar operation was performed for Cu-Ohmic contacts, where the circular Cu contacts with a diameter of about 1 mm and the thickness of about 70 nm were deposited at a pressure of about 4.35×10^{-7} kPa.

The electrical parameters' characterization is investigated by (*I*–*V*) measurements on FTO/CIGS/Al-Schottky structure using a Keithley 4200 CSC system and on SLG/CIGS/Cu structure by Hall Effect measurements in the temperature range of 300–438 K using Ecopia HMS-5300 equipment.

Results and discussion

SEM surface morphologies of CIGS1 and CIGS2 thin films are shown in Fig. 2a, b. As it can be seen, superimposed and faceted grains of different sizes were obtained and which proves their high-efficiency absorber nature [13].

One of the advantages of CSVT is the ability to produce thin film with structural properties allowing a good photovoltaic response. This evidence is shown by the experimental data obtained by EDS measurements (Table 1), which confirms that near-stoichiometric compositions were obtained.

To examine the crystalline state of the films, XRD measurements are carried out. Figure 3 shows their XRD patterns. The XRD spectra of CIGS1 (Fig. 3a) thin film exhibits diffraction peaks at about 27.18°, 44.95°, 53.26°, 65.34°, and 72.08° which correspond to intensity of a major peak (112) and the minor peaks such as (220/204), (312/116), (400/008), and (332/316), respectively, (JCPDS 35-1102). In the other hand, diffraction peaks of CIGS2 thin-film (Fig. 3b) appeared at 26.94°, 44.69°, 52.94°, 65.03°, and 71.83°. They correspond to intensity of a major peak (112) and the minor ones such as (220/204), (312/116), (400/008),

Table 1 Elemental composition of CIGS1 and CIGS2 thin films obtained by EDS

Material	Atomic composition (%)				
	Cu	In	Ga	Se	Ga/(Ga + In)
CIGS1	24.39	17.49	8.55	49.57	0.328
CIGS2	26.29	20.18	7.06	46.47	0.26

Fig. 2 SEM surface image of **a** CIGS1 and **b** CIGS2 thin films

Fig. 3 XRD spectra of **a** CIGS1 and **b** CIGS2 thin films

and (332/316), respectively. As observed, both films exhibit diffraction XRD patterns which are typically the same of chalcopyrite structure. However, a small shift of peak positions towards the lower angles is clearly visible when the substrate temperature increases. Shifts in XRD peak positions are caused by an increase in the Ga/(Ga + In) ratio which in turn could lead to a slight variation in the bandgap (Table 1) [12].

Electrical properties

Hall measurements have been done in the temperature range of 300–438 K on CIGS1 and CIGS2 thin films. The electrical parameters such as hole concentration (p), conductivity (σ) and mobility (μ) are extracted. Figure 4a, b illustrate p dependence on the temperature of the two samples. At high

temperature, the behavior of the semiconductor becomes intrinsic; therefore, the carrier concentration of holes is expressed as follows:

$$p = n_i = \sqrt{N_C N_V} \exp\left(-\frac{E_g}{2K_B T}\right) \quad (1)$$

where n_i is the intrinsic concentration, N_C is the effective density of states in conduction band (E_C), N_V is the effective density of states in valence band (E_V), K_B the Boltzmann's constant and T the temperature.

From the Arrhenius plots, $\ln(p)$ versus $1/T$, of CIGS1 and CIGS2, the obtained E_g is about 1.38 eV and 1.24 eV, respectively, which are higher compared to the standard E_g ($= 1.15$ eV). The two increases of E_g correspond to the excess of In which led to the increase of the open circuit voltage (V_{oc}) and to the decrease of short-circuit current (I_{sc}).

Fig. 4 Carrier concentration versus $1/T$ of **a** CIGS1 and **b** CIGS2 thin films

This in turn may lead to performance degradation of the thin film-based solar cell.

The electrical conductivity (σ) of the layers was measured as a function of temperature in the range (300–438 K). Results are summarized in Fig. 5. It is worth noticing that the conductivity is almost constant at low temperature, due to the ionization of nearly all impurities, whereas, a significant increase is observed at high temperature. This is due to the contribution of the band-to-band transitions which results in an increase in the free carrier's concentration.

The values of activation energy (E_a), at high and low temperatures, were determined from the Arrhenius plots, $\ln(\sigma)$ versus $1/T$, as illustrated in Fig. 6. For CIGS1 (Fig. 6a), the obtained E_a is about 239.4 meV, in the temperature range of 300–390 K. This level can correspond to the deep donor-level antisite defect In_{Cu} (0/+) below E_C , as it is demonstrated by Zhang et al. [20]. At high temperature range

(390–400 K), a deep level at 563.9 meV is deduced. This high energy situated near the midgap may correspond to a deep acceptor level Cu_{In} (2-/−) [20]. For CIGS2, (Fig. 6b), a defect transition level: $E(-/0) = E_V + 0.0727(2-/−)$ meV, in the temperature range (300–400 K), is deduced and assigned to a shallow acceptor defect V_{Cu} as explained in [20, 21]. Essentially, the p-type self-doping of CIGS is due to the low formation and shallow energy of this kind of defect. In the high-temperature range (400–438 K), the obtained deep acceptor level at $E(2-/−) = E_V + 584.2$ meV can correspond to the antisite Cu_{In} [20].

The mobility versus temperature is shown in Fig. 7a, b. In the temperature range (300–400 K), average values of about $1.83 \text{ cm}^2/\text{V s}$ and $1.77 \text{ cm}^2/\text{V s}$ were obtained, respectively, for CIGS1 and CIGS2. These low values are due to the increase in impurity scattering, which reduces the free carrier's movement. However, in the temperature range

Fig. 5 Temperature-dependent conductivity of **a** CIGS1 and **b** CIGS2 thin films

Fig. 6 Arrhenius plot of **a** CIGS1 and **b** CIGS2 thin films

Fig. 7 Temperature-dependent mobility of **a** CIGS1 and **b** CIGS2 thin films

Fig. 8 I – V characteristic of FTO/p-CIGS/Al Schottky diode in dark and at RT

(400–438 K) the value of the mobility increases with the increase of the temperature for both samples. This is mainly due to lattice scattering (phonons) that results in higher carriers moving speed, and therefore, the deviation becomes weak due to the Coulomb field.

Current–voltage characteristics

The (I – V) characteristic of the FTO/p-CIGS/Al junction in dark and at RT and studied under forward and reverse bias conditions acts like a Schottky diode which is confirmed by the obtained rectifying behavior as shown in Fig. 8.

In the forward bias, the (I – V) relationship of Schottky contact based on the thermionic emission (TE) theory [22] is given by Eq. (2):

$$I = I_s \left[\exp \left(\frac{q}{nK_B T} (V - R_s I) \right) - 1 \right] \quad \text{for } V \geq 3K_B T/q. \quad (2)$$

where I_s is the current saturation, q the electronic charge, V the bias voltage, R_s the series resistance and n the ideality factor.

The logarithmic form of the approximated version of Eq. (2) can be written as:

$$\ln I = \ln I_s + \frac{q}{nK_B T} (V - R_s I) \quad (3)$$

From Fig. 9a, which illustrates a semi-logarithmic plot of the (I – V) characteristic of the Schottky diode, the reverse current saturation is deduced at about 190 μ A.

The differentiation of Eq. (3) is given by:

$$\frac{dV}{d(\ln I)} = R_s I + \frac{nK_B T}{q} \quad (4)$$

Figure 9b shows a linear behavior of this variation. Hence, R_s and n are easily extracted. They are estimated to be 93.7 Ω and 3.47, respectively. These results are in good agreement with the work in [19]. The higher value obtained for n can be explained by the eventual potential drop and the recombination current through the interfacial layer [19, 22, 23].

Conclusion

Polycrystalline CIGS thin films have been grown by the close-spaced vapor transport (CSVST) technique onto two different substrates SLG and SLG/FTO. The investigations of structural and electrical properties of CIGS1 and CIGS2 thin films have been carried out in this work. The XRD spectra reveal that the films have a polycrystalline structure with a preferential orientation in the (112) plane. In addition, the slight shift of the peaks towards the lower angles was due to the slight energy bandgap variation. The latter is due to the increase of the Ga composition, as confirmed by the Ga/(Ga + In) ratios. Also, SEM studies have indicated faceted and superimposed grains of different sizes, which is typically of high-efficiency absorbers. Furthermore, EDS studies confirm that near-stoichiometric compositions are obtained. At low-temperature range, the obtained E_a is about 239 meV and 72.7 meV for CIGS1 and CIGS2 thin films, respectively. The former is assigned at the deep donor level In_{Cu} antisite and the latter at a shallow acceptor defect V_{Cu} . While, at high-temperature range, the obtained E_a is about 563.9 meV and 584.2 meV above E_v , for CIGS1 and CIGS2 thin-films, respectively, corresponding both to the deep acceptor level Cu_{In} antisite with the activity (2−/−). At high-temperature range, the mobility of the two thin films increases, due to the predominant lattice scattering (phonons) mechanism. While, at low-temperature range, the obtained mobility average values are about 1.83 $\text{cm}^2/\text{V s}$ and 1.77 $\text{cm}^2/\text{V s}$ for CIGS1 and CIGS2, respectively. This decrease in mobility is mainly due to the involved impurity scattering. The forward bias (I – V) characteristics at RT of the $\text{SnO}_2/\text{F}/\text{p-CIGS}/\text{Al}$ structure, based on thermionic emission (TE) theory have been also investigated. The high value found for n can be assigned to both the potential drop and the recombination through the interfacial layer.

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