Thermal Evaporated Undoped and Na-doped CuInS$_2$ with Copper Contact for Photovoltaic Applications

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Abstract- Undoped and Na-doped CuInS$_2$ powder has been synthetized by direct fusion of precursor elements. We have deposited those two materials in thin films on glass substrate and on copper layer by vacuum thermal evaporation method followed by an annealing in air atmosphere at 250°C and 450°C. We have investigated their structural, optical and electrical properties that show good results for photovoltaic applications. The undoped CuInS$_2$ layer exhibit an n-type conductivity whereas Na-doped CuInS$_2$ is p-type both on glass and on copper layer. X-ray analyses of the as deposited samples show amorphous structures. The annealed samples in air showed a crystallized CuInS$_2$ layer with a major peak of the (112) chalcopyrite phase with the presence of CuO and In$_2$S$_3$ impurity phases for the 450° annealed. Optical gap of both undoped and Na-doped CuInS$_2$ where between 1.4 and 1.6 eV, that is close to the optimal gap value 1.5 eV of the CuInS$_2$ suitable for a good absorption of solar spectrum. Electrical characterizations showed good ohmic contacts with low potential barrier height, and good ideality factor of respectively (0.75 eV, 1.37) for undoped and (0.66 eV, 1.27) for Na-doped CuInS$_2$/Cu contacts. Also, we observed a low value of series resistance 3.51 and 1.75 Ohms respectively that suppose a good current flow in the contact.

Keywords- Metal semi-conductor, CuInS$_2$/Cu, Na doping, structural, optical, electrical.

1. Introduction

Research in thin film solar cells is growing and new materials are being studied, but many researchers are still working on CuInS$_2$ solar cells because it’s still a promising material for solar cell with its optimal direct band gap of 1.5 eV that match’s well with the solar spectrum [1] and it’s high absorption coefficient of around $10^5$ cm$^{-1}$ [2]. Metal-semiconductors back contact plays an important role in the efficiency of the solar cell; it’s responsible of the flow and the collect of the generated electron-hole pairs responsible of the current produced by the cell. Many metals have been studied as back contacts with CuInS$_2$ in the literature such as Aluminium (Al), Carbone (C), Gold (Au), Silver (Ag), Molybdenum (Mo), Indium (In), Copper (Cu) [3-5]. Contacts on CuInS$_2$ made with aluminum were found to be Schottky as shown by J. M. Peza-Tapia et al. [4]. They reported in the same article good ohmic contacts with Ag and In metals with a low value of specific contact resistivity for the In contact with CuInS$_2$. D. C. Nguyen et al. [3] reported different efficiency for solar cell based on CuInS$_2$ with different metals back contacts (Al, Cu, Mo and Au deposited by rf sputtering and Carbon back contact by screen printing). Al and Au had the lower efficiency of 1.96 and 1.87 % respectively, back contact with Cu and Mo gave better efficiency (2.17 and 2.08 %) that make them good candidates for back contact in CIS solar cells.
Molybdenum back contact is the most used and has given good efficiency in CIS solar cells until today. Best efficiency of 12.5% has been achieved on Mo/CuInS$_2$/CdS/ZnO cell [6] but that type of cells contains toxic and cost elements. An important research goal in photovoltaic devices is the replacement of costly and toxic materials by nontoxic and cheap materials [7] to make clean, efficient and cheap solar cells available for most of the world population.

Copper is a low cost and non-toxic metal that has good electrical properties suitable for current conduction. He has an easy oxidation in air atmosphere, but used as back contact this property can be hidden by the top layer. That why many researchers have tried to use it as back contact in thin film solar cells based on CuInS$_2$.

The first report of copper as back contact with CuInS$_2$ was in 1998 and 2001 by J. Penndorf, M. Winkler et al. [8, 9], they first reached an efficiency of around 6%. Since then, many studies have been made to improve the quality of the CuInS$_2$/Cu back contact [10-15] by roll-to-roll process that was found to be a low-cost method able to produce large scale and event flexible cells but has the disadvantage of instability.

Vacuum thermal evaporation deposition has been found to be a good method to produce good quality and stable semiconductor thin films. M. B. Rabeh et al. [16] have obtained good quality CuInS$_2$ thin films by vacuum thermal evaporation followed by annealing in air atmosphere.

We report here, the structural, optical and electrical characterization of undoped and Na-doped CuInS$_2$ thin films and metal-semiconductor contact with Copper deposited by vacuum thermal evaporation followed by an annealing in air atmosphere at 250°C and 450°C. Na doping is performed in order to introduce acceptors atoms to convert the type of conductivity from n to p-type.

2. Experience

2.1. Synthesis of CuInS$_2$ powder

Undoped and Na-doped CuInS$_2$ powder was synthetized by direct fusion of precursor elements. For the Undoped, precursor elements Cu, In and S of 99.999% purity were sealed in a vacuum quartz tube in atomic stoichiometric proportions. The melt was heated in a programmable furnace first slowly at 20°C/h rate in order to avoid explosion due to sulphur vapor pressure, after a stabilization of the melt at 600°C for 24h, the complete homogenization was obtained after keeping at 1000°C for 48h then followed by a cooling at 10°C/h till 800°C before the natural cooling till ambient temperature. For the Na-doped, we added pure sodium element into the quartz ampoule containing the stoichiometric precursor’s elements Cu, In, S at 1 atomic percent (1 at. %) according to the good results obtained by M. Zribi et al. [17]. Crushed powder of both undoped and Na-doped CuInS$_2$ was used as raw materials for the thermal evaporation.

2.2. Contacts preparation

Thin film layers were grown by vacuum thermal evaporation on unheated glass substrates using a highly resistive tungsten crucible in a high vacuum evaporation system at a pressure of ~10$^{-5}$ Torr. We have deposited undoped and Na-doped CuInS$_2$ powder on unheated glass substrates in order to characterize the CuInS$_2$ layer. In order to form the metal semiconductor contact, around 100 mg of small copper pellets of 99.999% purity was evaporated on glass to form the copper layer. CuInS$_2$ was then evaporated on top of the copper layer in order to form the contact. The CuInS$_2$ layer was deposited on 80% of the copper surface in order to leave a free surface for the Cu-electrodes during electrical characterizations. To improve the crystallinity of the films and make sure we are dealing with good quality of CuInS$_2$, the samples were annealed in air atmosphere at 250°C and 450°C for 2h in a programmable furnace of Nabertherm type.

2.3. Contact characterizations

We have investigated the structural properties of the undoped and Na-doped CuInS$_2$ films on glass substrate and with copper contact by X-ray diffraction (XRD) using a D8 advance diffractometer with CuKa radiation. Optical transmittance and reflectance of the CuInS$_2$ layers on glass substrates were determined with a UV-VIS-NIR spectrophotometer of type Shimadzu 3100S in the range of 300-1800 nm. The type of conductivity of the CuInS$_2$ layer on glass substrates and copper was determined by the hot probe method. Current-voltage characterization of metal-semiconductor contacts was performed with an Agilent N6762A source-measure unit at ambient temperature.

3. Results And Discussion

3.1. Structural properties

Fig. 1 shows the XRD patterns of undoped CuInS$_2$ thin films as deposited, annealed at 250°C and 450°C in air atmosphere. We observe that the as deposited layer has an amorphous structure without any diffraction peak. This amorphous structure of CuInS$_2$ as deposited on unheated glass substrates has already been reported in previous work [18, 19]. After annealing at 250°C for 2h in air, we observe a growth of three peaks attributed to the CuInS$_2$ where the major peaks is the (112) at 2θ = 27.93° that indicate the majorly chalcopyrite phase of the film with a secondary InS (541) phase which disappear at 450°C. Two copper oxide CuO (-111) and (200) phases are observed at 450°C that can be explained by the reaction at high temperature between copper atoms and oxygen atoms present in the air atmosphere. The In$_2$S$_3$ may be related to the lack of copper that has been oxidized that left a Cu poor phase in the film. We noted a decrease in the intensity of the preferential (112) peak at 450°C that reflect a decrease of the crystallinity may be due to the presence of CuO and InS secondary phases in the material.
Fig. 1. XRD patterns of undoped CuInS$_2$ deposited on glass substrates.

Fig. 2 shows the XRD patterns of the Na-doped CuInS$_2$ on glass substrates as deposited and annealed at 250°C and 450°C in air atmosphere. The as deposited sample exhibit an amorphous structure like the undoped but the 250°C annealed one is also amorphous may be due to the presence of Na atoms in the structure who have difficulties to integrate the sites of the matrix may be due to the great value of the radius of Na atom (190pm) related to Cu atomic radius (128pm). The 450°C annealed sample shows a mixture of two chalcopyrite phases CuInS$_2$ and CuIn$_5$S$_8$ with the preferential peak for the CuInS$_2$ (112). The presence of the CuIn$_5$S$_8$ as a minor phase in Na doped CuInS$_2$ has already been reported in the literature as impurity phase [20, 21]. Another explanation could be that Na atoms integrate the matrix and occupied Cu lattices sites and leave Cu vacancies that lead to CuIn$_5$S$_8$ phase.

Fig. 3 shows XRD patterns of undoped CuInS$_2$ deposited on copper layer. An amorphous CuInS$_2$ phase is observed on the as deposited samples as already seen in XRD patterns of CuInS$_2$ on glass substrate. But, there are two peaks in the patterns that has been identified as Cu (111) and Cu (200) at $\theta = 43.39$ and $50.58^\circ$ respectively. This confirms the presence of a copper layer in the structure. After annealed at 250°C, we observed the growth of CuInS$_2$ peaks with the (112) one that is preferential. But still the copper peaks are observed due to the semi crystallized CuInS$_2$ layer. In the 450°C annealed sample, there are no copper peaks indicating a good crystallization of the CuInS$_2$ layer with its preferential chalcopyrite (112) peak that hides the copper layer from the X-rays. We noted here the preferential (112) peak of CuInS$_2$ of the 450°C annealed sample is more intense than the 250° annealed one, contrary to the case of the CuIn$_5$S$_8$ layer deposited on glass substrate where the (112) peaks was less intense at 450°C. This may be due to the diffusion of copper atoms from the copper under layer in the CuInS$_2$ layer that compensate the lack of Cu and ameliorates the crystallinity of the CuIn$_5$S$_8$ layer. We noticed here the benefit effect of the copper under layer which plays a copper atoms tank role for the CuInS$_2$. Copper oxide impurities due to the oxidation in air atmosphere that contribute to the decrease in crystallinity.

Where $\lambda$ is the X-ray wavelength of 1.5418 Å, $\theta$ is the Bragg diffraction angle and $\beta$ is the Full Width at Half Maximum (FWHM).

The values of the crystallites sizes and their correspondent FWHM are listed in table 1 were we observed a decrease of the crystallite sizes with the annealing temperature.

**Table 1.** Bragg angles, FWHM, grains sizes, for undoped and Na-doped CuInS$_2$ as deposited and annealed at 250°C and 450°C.

<table>
<thead>
<tr>
<th>CuInS$_2$ samples</th>
<th>Annealed T(°C)</th>
<th>Bragg Angles (°C)</th>
<th>FWHM</th>
<th>Grains sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un doped</td>
<td>As dep.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>250°C</td>
<td>27.82</td>
<td>0.117</td>
<td>122.02</td>
</tr>
<tr>
<td></td>
<td>450°C</td>
<td>27.93</td>
<td>0.267</td>
<td>53.43</td>
</tr>
<tr>
<td>Na doped</td>
<td>As dep.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>250°C</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>450°C</td>
<td>27.70</td>
<td>0.334</td>
<td>42.71</td>
</tr>
</tbody>
</table>

The size of the crystallites in the grains were estimated by the Debye-Scherrer formula [22]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$ (1)
The same observation is done with the XRD patterns of Na-doped CuInS₂ on copper substrate on fig. 4 were the as deposited and the 250°C annealed sample shows an amorphous structure with the presence of Cu (111) peak. The Cu peaks disappear after annealed at 450°C and the CuInS₂ (112) peak is major. We also have the CuO (111)(200) and the In₃S₈ (222) phases as for the Na-doped CuInS₂ on glass substrate. We noticed the absence of CuInS₈ phases on the 450°C annealed sample comparatively to the sample on glass substrate may be due to the diffusion of Cu atoms coming from the Cu layer that has form a Cu-rich layer compensating the lack of Cu atoms in the CuInS₈ phases. We note here again another benefit effect of the copper under layer on the CuInS₂ thin film.

3.2. Optical properties

We have measured the optical transmittance and reflectance in the range of 300 nm to 1800 nm for the as deposited and annealed samples of undoped and Na-doped CuInS₂ on glass substrates (fig. 5, fig. 6). The reflectance for both undoped and Na-doped are in the range of 10 to 40%, while the transmittance rise till 80% and 88% for the as deposited and the 250°C annealed samples and just to 60% and 70% for the 450°C annealed undoped and Na-doped samples respectively. We noted a loss of oscillations for the 450°C annealed undoped sample that confirm the decrease of crystallinity observed in the XRD patterns due to the secondary oxide phases. All the Na-doped spectra shows oscillations even the 450°C annealed one sign of a good homogeneity of the film. The absorption coefficients of all the CuInS₂ samples were in the range of 10⁵ cm⁻¹ that is suitable for high solar spectrum absorption.
The optical band gap was calculated by the Tauc model [24] and the Davis and Mott model [25] in high absorbance region given by the relation:

\[(\alpha h \nu)^n = A(h \nu - E_g)\]  

(2)

Where \(A\) is a constant, \(h \nu\) the photon energy, \(\alpha\) is the absorption coefficient and \(E_g\) the optical band gap. \(n\) is a coefficient depending on the type of transition allowed in the film \(n = 2\) for a direct transition allowed and \(n = \frac{1}{2}\) for an indirect transition allowed. The plot of \((\alpha h \nu)^n\) vs \(h \nu\) yields a straight line that indicate in the abscise axis the average value of the band gap. Fig. 7 and fig. 8 show the plots of \((\alpha h \nu)^2\) vs \(h \nu\) for all the undoped and Na-doped samples. We noted a decrease of band gap value with the annealing temperature due to the improvement of the crystallinity of the films. Values are between 1.3 eV and 1.6 eV around the optimal band gap value of the CuInS\(_2\) suitable for solar spectrum absorption for photovoltaic applications.

The hot probe method was used to determine the type of conductivity of the major carrier for the undoped and Na-doped CuInS\(_2\) on glass substrate. The undoped CuInS\(_2\) layer was n type and the Na-doped was p type either on glass substrates than on copper layer. They can then be combining with p or n-type oxide transparent conductor in photovoltaic solar cell applications.

### 3.3. Electrical properties

We have measured the current-voltage (I-V) characteristic of the contact with our source measure unit at ambient temperature. The I-V curves are shown on fig. 9 and fig. 10 for the undoped and the Na-doped CuInS\(_2\) contact with copper respectively. Both curves showed linear characteristic that means a good ohmic contacts suitable for photovoltaic back contacts.

**Fig. 9.** current-voltage characteristic of the undoped CuInS\(_2\) contact with copper.

**Fig. 10.** Current-voltage characteristic of the Na-doped CuInS\(_2\) contact with copper.

The saturation current has been determinate by our measurement unit as the current value when \(V = 0\). The values are listed in TABLE 2. They are in the range of \(10^{-6}\) to \(10^{-5}\) (A) respectively for the undoped and the Na-doped CuInS\(_2\) contact.

The potential barrier height, the ideality factor and the series resistance of the contact have been investigated by the Schottky model [26] assuming the thermionic emission
is the predominant mechanism of conduction in the contact that is usually for and ideality factor between 1 and 2 [27].

The relationship between the current I and the voltage V is given by the formula:

$$I = I_s \left( \exp \left( \frac{qV}{nkT} \right) - 1 \right)$$

(3)

Where $I_s$ is the saturation current, $q$ the electron charge, $n$ the ideality factor, $k$ the Boltzmann constant and $T$ the temperature.

The potential barrier height $\phi_b$ is given in the expression of the saturation current $I_s$:

$$I_s = A A' T^2 \exp \left( - \frac{q \phi_b}{kT} \right)$$

(4)

Where $A$ is the area of the contact, $A'$ the Richardson constant of the semiconductor material.

The potential barrier values are respectively 0.75 and 0.66 eV for undoped and Na-doped CuInS$_2$ contacts. These barrier values are low, that suppose the existence of a weak barrier of potential between the CuInS$_2$ layer and the copper that suppose a good flow of current in the contact.

The values of the ideality factor $n$ where obtained from the slope of the linear region of the plot of $Ln(I)$ vs $V$ in the low voltage region. The ideality factor values are 1.37 and 1.27 respectively. They are between 1 and 2 that confirm the use of the Schottky thermionic emission theory and they are close to the ideal value 1 that supposes a good diode contact fabrication and few defects in the contact.

We have determinate the series resistance of the contacts that gives an indication of the opposition of the current flow in the contact due to the contact and the electrodes.

The series resistance is expressed by the relation:

$$\frac{dV}{dLn(I)} = R_s + \frac{nkT}{q}$$

(5)

$R_s$ is the slope of the linear region of the curve of $V/\ln(I)$ vs $I$. The values obtained are 3.51 and 1.75 $\Omega$. This supposes a good flow of charges between the electrodes and the contact layers that is good for photovoltaic applications where we need to collect the maximum of the electrons-holes pairs generated in the cell to produce current.

**Table 2.** Saturation current, potential barrier height, ideality factor and series resistance of undoped and Na-doped CuInS$_2$ contact with copper.

<table>
<thead>
<tr>
<th>Contact material</th>
<th>$I_s$ (A)</th>
<th>$\phi_b$ (eV)</th>
<th>n</th>
<th>$R_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped CuInS$_2$/Cu</td>
<td>3.75 $\times 10^{-6}$</td>
<td>0.75</td>
<td>1.37</td>
<td>3.51</td>
</tr>
<tr>
<td>Na-doped CuInS$_2$/Cu</td>
<td>7.02 $\times 10^{-5}$</td>
<td>0.66</td>
<td>1.27</td>
<td>1.75</td>
</tr>
</tbody>
</table>

4. Conclusion

We have synthetized undoped and 1% at. Na-doped CuInS$_2$ material by direct fusion of precursor elements and we have made metal semiconductor contacts with copper metal layer by thermal evaporation followed by an annealing in air atmosphere at 250°C and 450°C. We have characterized the undoped and the Na-doped CuInS$_2$ layer on glass substrate and the contact with copper. The results of the characterization of the CuInS$_2$ layer on glass substrates gave thin film with band gap value between 1.4 and 1.6 eV and absorption coefficient in the range of $10^5$ cm$^{-1}$ that are suitable as absorber layer for photovoltaic applications. Structural investigations of the undoped and Na-doped CuInS$_2$ layer on glass showed an amorphous structure for the as deposited samples but the 450°C annealed one were crystallized with the major peak attributed to the (112) CuInS$_2$ chalcopyrite phase. The structural properties of the contacts with copper shown the same patterns with the presence of the Cu (111) and (200) peaks for the as deposited and the 250°C annealed samples. The Cu peak disappears in the 450°C annealed pattern and the CuInS$_2$ (112) peak is still major. The electrical studies showed good result for the potential barrier height, the ideality factor and series resistance. The low value of the barrier supposes an easier passage of charges between Cu metal and CuInS$_2$ semiconductor. The ideality factor close to 1 let suppose a good contact fabrication with few defaults. The low value of series resistance let think of a good flow of charges between the electrodes and the layers of the contact. All those properties make the undoped and Na-doped CuInS$_2$ thin films good n and p-type absorber layers and metal back contact with copper could be good candidate for photovoltaic solar cell applications.

**References**


