

# Comparative Study Between CdS/Cu(In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> and CdS/Cu<sub>2</sub>ZnSn(S<sub>y</sub>Se<sub>1-y</sub>)<sub>4</sub> Structures

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## Abstract

We presented in this paper a comparative study between CdS/Cu(In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> and CdS/Cu<sub>2</sub>ZnSn(S<sub>y</sub>Se<sub>1-y</sub>)<sub>4</sub> Structures based solar cells. We investigated the effect of both Gallium (Ga) and sulfur (S) contents on the electrical performances, the mismatch strain at the interface buffer/absorber and the conversion efficiency of CdS/CIGSse structure and only the influence of the sulfur component on the CdS/CZTSSe on the same parameters above mentioned. The obtained results was analysed and compared, it will be shown that the efficiency of the CdS/CZTSSe structure is significantly lower than that of the CdS/CIGSse one, the same think is observed for the V<sub>oc</sub> of the CdS/CZTSSe structure which still lower than the expected value and than that of the CdS/CIGSse. It was also been demonstrated that the control of composition in the two structures can be optimized in order to get best efficiencies with optimal performances.

**Keywords:** CIGSse thin film, CZTSSe thin film, solar cell.

## 1. INTRODUCTION

In order to reduce pollution level in the world and the greenhouse effect humans should consider the use of solar energy to preserve the safety of the planet. Nowadays, solar market is dominated by wafer based silicon technology [1]. A number of materials have been investigated for the development of next generation of low cost and high efficiency solar cell such us CIS, CdTe, CIGS, the solar cells based on these thin films materials are known as a promising devices in photovoltaic technology and reached the level of mass production [2]. The efficiencies of devices based on CIGSse absorbers exceed 20% [3]. However, there still a large margin of improvement to reach the maximum theoretical efficiency of ~ 33% for an absorber of E<sub>g</sub> = 1.15 eV [4]. In addition, because of the supply for Indium, Gallium and Tellurium and the toxicity of Cadmium and Selenium, it is necessary to develop alternative light absorber material that are low cost, non toxic and easily available. Cu<sub>2</sub>ZnSn(S<sub>x</sub>S<sub>1-x</sub>)<sub>4</sub> thin film has been extensively studied as a possible alternative absorbers to CuInGa(S<sub>x</sub>Se<sub>1-x</sub>)<sub>2</sub> thin film solar cell due to its low toxicity, the abundances of its constituents and its very promising properties. The highest efficiency up to 12.6% was achieved by solution process

CZTSSe solar cell by IBM as a world record [5]. That remains very less than the record achieved by the devices based on Cu(In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> thin films, that is why it becomes very important to understand the reasons that hinders the efficiency and the electrical performances of devices based on CZTSSe thin films. In this work, a comparison study between the performances of CdS/Cu(In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> and CdS/Cu<sub>2</sub>ZnSn(S<sub>y</sub>Se<sub>1-y</sub>)<sub>4</sub> Structures based solar cells is presented due to the similarity of CIGSse and CZTSSe materials systems, the effect of grading band gap of CIGSse and CZTSSe materials on Voc, J<sub>sc</sub>, FF, efficiency and mismatch strain at the Buffer/absorber interface is investigated for each structure. The main of this simulation work is to get a better understanding of the influence of the control composition of the absorbers materials contents on the efficiency and the electrical performances of the cells based on these materials, especially for the CZTSSe material which presents some limitations that need to be improved compared to the CIGSse device as regards the efficiency and V<sub>oc</sub>.

## 2. Theoretical Approach

The simulated solar cells follow the standard device Mo(800nm)/CIGSse or CZTSSe(3µm)/CdS(50nm)/ZnO(80nm)/ITO(220nm)/Ni-Al grids / MgF<sub>2</sub>(100 nm) [6]. In CIGSse absorber, high efficiency is achieved by controlling the band gap profile which can be tuned by changing x=Ga/Ga+In and y=S/S+Se ratios respectively [7]. The following expression of the band gap dependency for Cu (In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> is derived from the combination of several previous work[8]:

$$E_g(x, y) = -0.14x^2y + 0.14x^2 + 0.39xy + 0.15y^2 + 0.35x + 0.49y + 1.04 \quad (1)$$

However we consider in this work that Cu<sub>2</sub>ZnSn(S<sub>y</sub>Se<sub>1-y</sub>)<sub>4</sub> depends only on the sulfur ratio. The band gap in this case is given by [9]:

$$E_g(x) = 1.51x + 1.02(1-x) + 0.08x(1-x) \quad (2)$$

The total photo generated current density is given by the sum below [10]:

$$J_{ph}(\lambda) = J_n(\lambda) + J_p(\lambda) + J_w(\lambda) \quad (3)$$

$J_n(\lambda)$ : electron current density of the front region.  
 $J_p(\lambda)$ : hole current density of the base region.  
 $J_w(\lambda)$ : current density in the depletion region.

The total illumination current density is written as:

$$J_{ph} = \int_{\lambda_{\min}}^{\lambda_{\max}} q \cdot F(\lambda) \cdot EQE(\lambda) d\lambda \quad (4)$$

$q$ : elementary charge.  $F(\lambda)$ : photon flux of the incident spectrum.  $EQE(\lambda)$ : external quantum efficiency

The open circuit voltage  $V_{oc}$  is expressed as [11]:

$$V_{OC} = \frac{nkT}{q} \ln \left( \frac{J_{ph}}{J_0} + 1 \right) \quad (5)$$

$n$ : ideality factor.  
 $J_0$ : dark current density.

The current voltage  $J(V)$  characteristic of the solar cell is described by [10]:

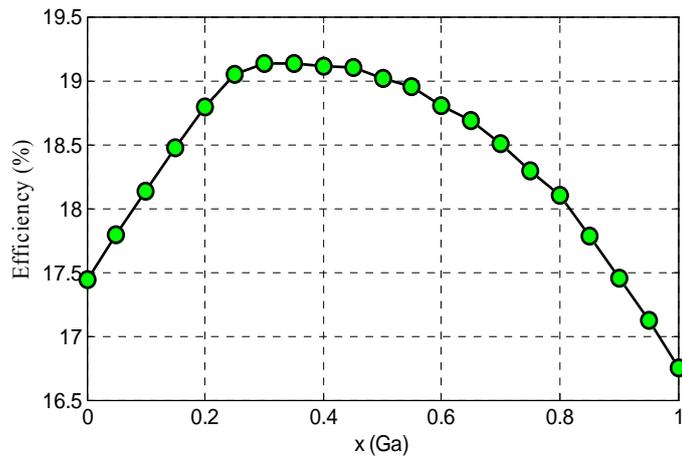
$$J(V) = J_{ph} - J_s \left( \exp \frac{qV}{nKT} - 1 \right) \quad (6)$$

$J_s$ : saturation current.

### 3. Results and Discussion

#### 3.1. Gallium effect on $Cu(In_{1-x}Ga_x)Se_2$ device performances

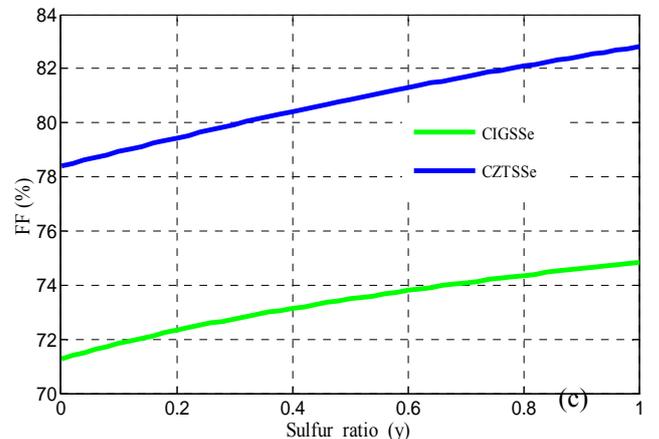
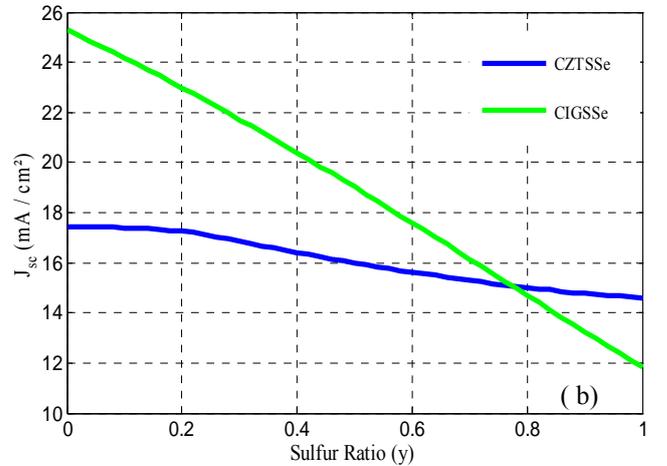
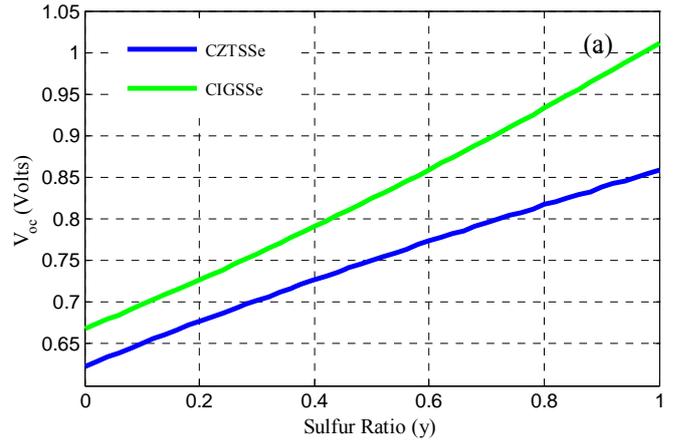
We have studied in a previous work the effect of the Gallium concentration on the performances of the  $CdS/Cu(In_{1-x}Ga_x)Se_2$  based solar cell with no sulfur content in the absorber material (pure Se). The results show that all the performances vary with the augmentation of the Gallium content from 0% to 100% in the absorber alloy. We have noted an augmentation of  $V_{oc}$  from 0.601V to 0.894V and FF from 76.92% to 81.69% and a diminution of  $J_{sc}$  from 26.21mA/cm<sup>2</sup> to 15.96 mA/cm<sup>2</sup>. Figure 1 displays the efficiency variation as the augmentation of Ga in the CIGSe material.

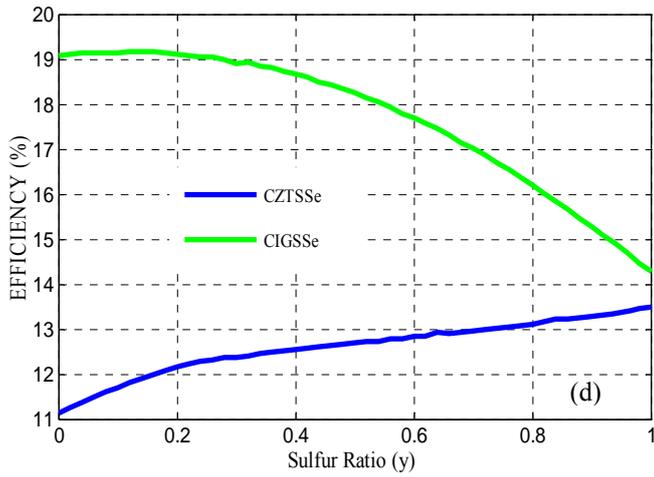


**Fig1.** Efficiency of CIGSe cell as function of Ga

The obtained curve reveals that we have an increase of efficiency from 17.44% to the maximum value of 19.12% which corresponds to  $E_g = 1.17eV$  when  $x$  rises from 0% to 30% but begins to decrease after until the value of 16.75% for 100% of gallium.

For the rest of our comparison study, we will fix the concentration of Gallium at 30% in order to base our comparison work on only the effect of sulfur introduction on the  $CuInGa(S_ySe_{1-y})_2$  and  $Cu_2ZnSn(S_ySe_{1-y})_4$  based cells. Figure 2 shows the effect of the growth of the sulfur concentration on the electrical performances of CIGSSe and CZTSSe absorbers based cells. Figure 2 (a) reveals that  $V_{oc}$  increases in the two devices when the sulfur component augments from 0.622V to 0.858V for CZTSSe device and from 0.668V to 1.011V for CIGSSe device that means that the augmentation of  $V_{oc}$  is greater in the CIGSSe solar cell. In addition its value is always lower in CZTSSe device than that of the CIGSSe device during the augmentation of sulfur.



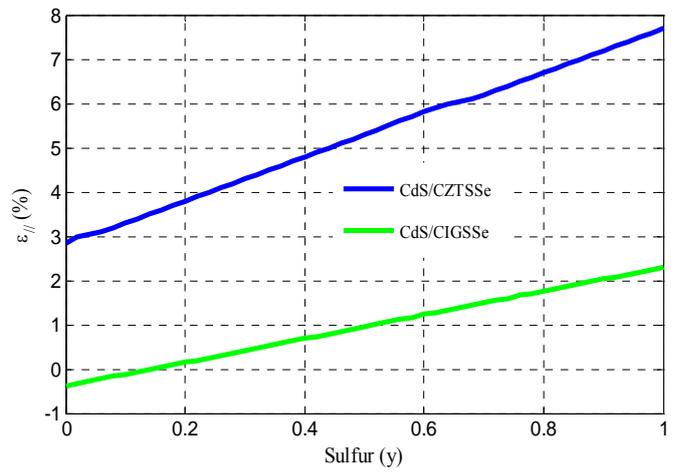


**Fig2.** (a):  $V_{oc}$ , (b):  $J_{sc}$ , (c): FF, (d): Efficiency of CIGSSe and CZTSSe based cells as functions of Sulfur composition  $y$ .

The reason for such low open circuit voltage is related to defects in absorber material [12], in addition, CZTSSe has been characterized with a more spatially dependent defect profile than CIGSSe. Figure 2 (b) represents the behavior of  $J_{sc}$  in both devices when the concentration of Sulfur augments in the absorbers. It appears clearly that  $J_{sc}$  declining faster in the CIGSSe based cell comparing to the CZTSSe one, we note a loss of 13.46 mA/cm<sup>2</sup> for the first device and a loss of 2.86 mA/cm<sup>2</sup> only for the second one. We deduce that  $J_{sc}$  in CIGSSe based cell is more sensitive to the introduction of the sulfur content than that in CZTSSe based cell. The increase in  $V_{oc}$  and decrease in  $J_{sc}$  is due to the increased band gap. Figure 2 (c) shows that FF of CIGSSe solar cell is more significant than that of CZTSSe one and augments in both devices with the increase of sulfur ratio, from 78.39% to 82.82% for CIGSSe device and from 71.28% to 74.83% for CZTSSe device. Figure 2 (d) depicts the efficiency of both CIGSSe and CZTSSe based cells as function of sulfur ratio. This concerns CIGSSe device, when the concentration of Sulfur increases from 0% ( $E_g = 1.17\text{eV}$ ) to 25% ( $E_g = 1.35\text{eV}$ ) the value of efficiency is maintained around 19% but beyond 30% of sulfur the conversion efficiency runs down to 14.27% for 100% of sulfur. However, mixing sulfur with selenium in CZTSSe absorber contributes to improve efficiency from 11.14 % to 13.48%.

### 3.2. Sulfur impact on the mismatch strain

Figure 3 illustrates the variation of the strain at the interface between the buffer layer and the absorber layer in CdS/CIGSSe and CdS/CZTSSe structures as function of sulfur ratio  $y$ . The strain at the CdS/CZTSSe is always extensive and vary from 2.9% to 7.7% that means that the deformation becomes more significant when the concentration of sulfur increases. However at the CdS/CIGSSe interface the lattice matching occurs at 14% of sulfur in the CIGSSe composition, below this value the strain is compressive and vary from -0.38% to 0% and above the strain becomes extensive and augments until 2.3%. We deduce that the CdS material is more appropriate buffer material for the CIGSSe absorber than for the CZTSSe. We suggested after analyzing the results obtained that 25% of sulfur in CIGSSe absorber is sufficient to maintain the efficiency at 19.1% and it allows at the same time the increase of the band gap at 1.35eV which coincides with the maximum of irradiance spectrum.



**Fig 3.** Mismatch strain at CdS/CIGSSe and CdS/CZTSSe interfaces as function of  $y$  composition.

For CdS/CIGSSe structure, 30% of Gallium and 25% of Sulfur, we obtain the following optimal performances, a conversion efficiency of 19.1% with  $V_{oc} = 0.743\text{V}$ ,  $J_{sc} = 22.35\text{mA/cm}^2$ , FF = 79.69% and a deformation of  $\epsilon_{||} = 0.28\%$ .

Which concerns the CdS/CZTSSe structure, mixing sulfur with selenium contributes to improve efficiency but contributes to increase the deformation at the interface buffer / absorber. For the same concentration of sulfur as the previous device, the CdS/ CZTSSe structure realizes an efficiency of 12.30% with  $V_{oc} = 0.689\text{V}$ ,  $J_{sc} = 17.08\text{mA/cm}^2$ , FF = 72.54% and  $\epsilon_{||} = 4.1\%$ .

Comparing to the performances of CdS/CIGSSe device, we note a smaller  $V_{oc}$ , which confirms what has been reported in the literature where low open circuit voltages is commonly seen in CZTS, CZTSSe and their mixing alloys CZTSSe, the reason of that may be caused by short minority carriers life times related to defects in the absorber which reduces also the probability of collection carriers and diminishes the short circuit current. Some previous works have reported that  $V_{oc}$  is limited by low built-in potential  $V_{bi}$  [13].

A high carrier concentration should reduce the photovoltaic properties due to the low mobility of electrons in the absorber [14]. Despite the improvement of the efficiency its value still very far from that obtained by CdS/CIGSSe device because of the recombination at the buffer/absorber interface and high defect densities. Our study demonstrate that CdS must be replaced by a more appropriate buffer which presents a better lattice matching with CZTSSe absorber in order to minimize interface recombination and avoid the toxicity of Cd. Among the proposed solutions to improve efficiency and increase  $V_{oc}$ , we find the use of spatial graded band gap absorber, back, front or double graded, two layers d-type absorber was proposed to increase  $V_{oc}$ . A good understanding of the defects nature is recommended and a good control of techniques of deposition is necessary to obtain high quality absorbers

## 4. Conclusion

In this work we have simulated the photovoltaic performances of CdS/  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{S}_y\text{Se}_{1-y})_2$  and CdS/  $\text{Cu}_2\text{ZnSn}(\text{S}_y\text{Se}_{1-y})_4$  based devices. The aim of the work was to show the influence of the composition of the absorbers in both solar cells on the electrical parameters and the deformation at the interface buffer/absorber. The observation of the behavior of performances with the variation of the alloys composition

allowed us to optimize the concentration of Gallium and sulfur in the CIGSSe material and the sulfur ratio in the CZTSSe material in order to get the best efficiencies with optimal electrical performances and optimal deformation between buffer and absorber layers. We have found that for 30% of Gallium and 25% of sulfur in CIGSSe absorber we get an efficiency of 19.1% with  $V_{oc} = 0.743V$ ,  $J_{sc} = 22.36mA/cm^2$ ,  $FF = 79.69\%$  and an extensive strain of 0.28% at  $E_g = 1.35eV$  which is close to 1.4eV where we have the maximum of irradiance. For the same concentration of sulfur, CdS/CZTSSe device have realized an efficiency of 12.30% with  $V_{oc} = 0.689V$ ,  $j_{sc} = 17.08mA/cm^2$ ,  $FF = 72.54\%$  and  $\epsilon_{//} = 4.1\%$ . The comparison between the results showed us that it is necessary to improve  $V_{oc}$ , efficiency and strain in CZTSSe based solar cell in order to be able to replace cells based on CIGSSe in the future.

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