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Impact of the secondary phase ZnS on CZTS performance solar cells

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Abstract— **In the present study, ultra-thin layer ZnS is inserted in the structure of standard solar cell between CdS buffer layer and CZTS absorber layer to represent the Second Phase (SP) often forms on the top of CZTS. The impact of this layer on the performance of CZTS solar cells is illustrated by the diverse results obtained by simulation using SCAPS-1D. The formation of ZnS on the CZTS surface has harmful effects on the solar cells parameters where the conversion efficiency (η) decreases by 2%. When varying thickness of ZnS SP of 2% to 20% corresponding of the total absorber layer the efficiency decreases by about 0.65%. The ZnS SP can deteriorate the photovoltaic power conversion efficiency from 10.2% to levels of 8.8%, depending on the material buffer layer and the thickness of ZnS SP. Using the ZnS as buffer layer mitigates harmful effects of the ZnS secondary phase forms on the top of CZTS absorber layer.**

Keywords— **CZTS; Solar cell; Secondary Phases; CdS; ZnS; SCAPS-1D.**

I. Introduction

Absorber kesterite material $CuZnSnS_4$ (CZTS) has been recently attracted for fabrication of thin film solar cells due to earth-abundant, low-cost, non-toxic elements, tunable band gap energy (from 1.48 to 1.63 eV) closer to the optimum band-gap value of 1.45 eV for a single junction solar cell [1], economic process ability like spray deposition [2,3], sol-gel and spin coating [4,5],and exceptionally high absorption coefficient (over 10^4 cm^{-1}) [6]. But, despite the advantages owned by this material, the solar cells based on the CZTS exhibit relatively weak conversion efficiencies, CZTSSe solar cell with efficiency of 12.6% [6] and only 9.1% of the CZTS solar cell [7] due to our understanding of CZTS based solar cell which is relatively limited compared to other cells, like CIGS, CdTe and Silicon thin film. The CZTS cells are still suffering from low electronic properties mainly due to the high carrier recombination both in the bulk and in the interface between absorber (CZTS) and the buffer layers where atomic arrangement is disturbed severely, add to the secondary phases of ZnS, SnS and Cu_2SnS_3 appear in CZTS films, at both the front surface of the CZTS films and the back contact interface [8, 9]. These secondary phases can be detrimental to the device performance, as the SnS phase has lower bandgap than CZTS phase, and could modify the interface properties, while ZnS phase can block current flow and introduce dead areas [10]. According to the recent studies, ZnS is the main secondary phase in the Cu_2ZnSnS_4 layer obtained from a sulphurised Zn/CuSn metallic stack. The excess Zn trends to diffuse from back contact region to top surface of Cu_2ZnSnS_4 layer accumulating in the form of ZnS [11]. The solar cell with a higher Zn concentration shows a large quantity of isolated ZnS grains at Cu_2ZnSnS_4 top surface which is close to CdS/Cu_2ZnSnS_4 hetero-junction interface [12], the ZnS phase in CZTS is predicted to be resistive barriers for carriers, which is generally deleterious to solar cell performance [13,14].

The purpose of this work is to study, using SCAPS-1D [15] simulation package, the impact of the secondary phase ZnS on the photovoltaic output parameters of CZTS solar cells. We examine the influence of ZnS layer thickness, the doping concentration as well as the effect of ZnS as buffer layer in the presence of the ZnS second phase.

II. Device structure and simulation details

The standard devices based CZTS consist of a thin-film multilayer deposited on soda lime glass (SLG), Mo/MoS_2/CZTS/ CdS/i-ZnO/ZnO:Al. A back metal electrode Molybdenum (Mo), MoS_2 formed between absorber and back contact; a p-CZTS absorber layer, an n-type buffer layer, typically CdS to create the junction of the solar cell, a doped ZnO layer (TCO), and ZnO:Al transparent front contact. Metallic Ni/Al contact grids complete the cell.

In this study, we insert a thin layer between the buffer layer CdS and the absorber CZTS, Fig.1, to represent secondary phase ZnS generally formed on the top of absorber layer [16].

Numerical simulation is an effective way to test and predict the thin film solar cell performance [15]. In this work, we have used a simulation program called Solar Cell Capacitance Simulation in 1 Dimension (SCAPS-1D) to predict the changes to CZTS based solar cell performance that are introduced by the presence of the secondary phase ZnS at the top of CZTS absorber.

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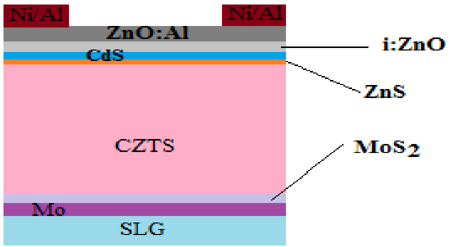

Fig.1 Schematic structure of CZTS based thin-film solar cells (layer thicknesses not to scale)

This software tool is a one dimensional solar cell device simulator, developed at the University of Gent [17], allows the definition of thin-film solar cell devices stacks of layers with a large set of parameters and solves for each point the fundamental solar cell equations: the Poisson equation and the continuity equations for electrons and holes. Definable parameters include the thickness, doping, defect and interface–state densities and cross-sections, optical absorption coefficient, band-gap and electron affinity. The Shockley-Read-Hall (SRH) model is used to describe the recombination currents in deep bulk levels. All the bulk defects layers are positioned at the mid band gap [17]. For the simulation under illumination the AM1.5 standard spectrum is used and the cell operating temperature is set at 300 K. The series and shunt resistances are taken in to account in this study with values respectively fixed at 0.96 and 670 $\Omega.cm^{-2}$ [18].

TABLE I
Input Parameter Values For The Simulation Of CZTS Solar Cells With SCAPS-1D.

Layer properties					
	CZTS	CdS	ZnS	MoS_2	i:ZnO
W(nm)	700	var	Var	100	200
E_g (eV)	1.50	2.4	3.7	1.6	3.3
χ (eV)	4.1	4.215	4.5	4.2	4.4
$\varepsilon/\varepsilon_0$	7	10	10	13.6	9
N_c (cm^{-3})	$2.2*10^{18}$	$2.2*10^{18}$	$1.8*10^{18}$	$2.2*10^{18}$	$2.2*10^{18}$
N_v (cm^{-3})	$1.8*10^{19}$	$9.1*10^{18}$	$1.8*10^{19}$	$1.8*10^{19}$	$1.8*10^{19}$
ν_n (cm/s)	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$
ν_p (cm/s)	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$	$1*10^7$
μ_n (cm^2/Vs)	60	100	100	100	100
μ_p (cm^2/Vs)	20	25	25	25	25
Doping (cm^{-3})	Var (A)	$1*10^{17}$(D)	Var (D)	$1*10^{16}$ (A)	$1*10^{18}$

TABLE II
Measured and Simulated Solar Cell J-V Parameters.

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Simulation With ZnS	0.7265	20.2895	60.07	8.85
Simulation W/o ZnS	0.7322	22.2277	61.18	9.96
Experimental [18]	0.683	20.7	62.5	8.8

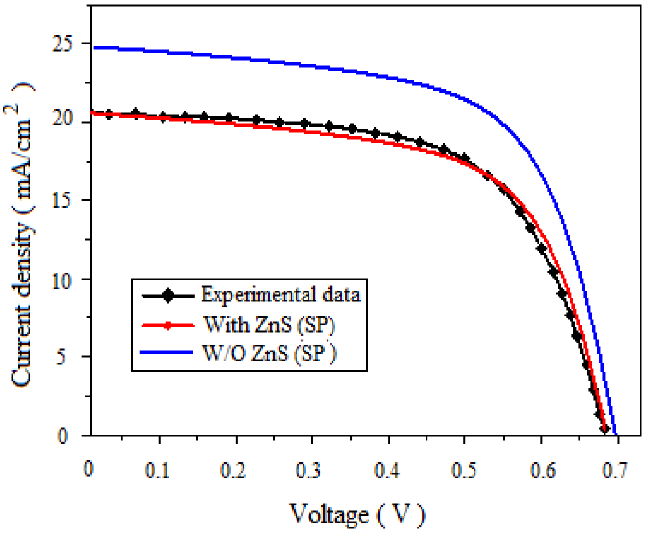

Fig.2 Comparison between the (J-V) curves for the simulated and the reported experimental data [21]

III. RESULTS AND DISCUSSION

The current-voltage (J-V) results from simulation using the parameters given in table I, with and without ZnS Secondary Phase (SP) are compared with measurement data from [18] in Fig.2. The results show that the measured JV curve is very well reproduced by the parameters model, with SP, which validates our set of parameters as a baseline for simulating the impact of the SP parameters on solar cell performance. The JV parameters from simulations and measurements are displayed in table II.

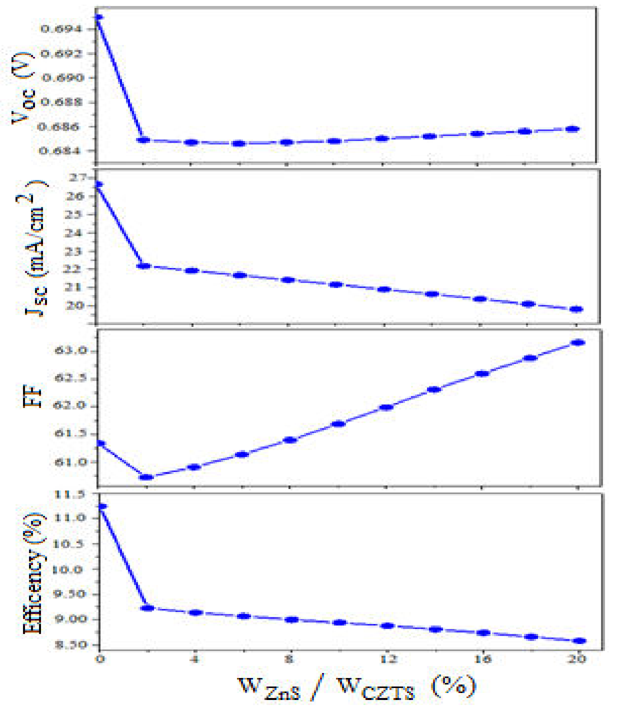

Fig.3 Dependence of FF and η, J_{sc} and V_{oc} on the thickness of the secondary phase ZnS.

A. Modeling with various ZnS thickness

One important parameters having a great impact on the solar cells performance, is the thickness of layers constituting the device. In this part, we have investigated the effects of the ZnS SP layer thickness on the device electrical parameters as termes of efficiency (η), open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF). This is shown in Figure 3. The other layers properties are kept constant and the doping of ZnS layer is fixed at 10^{16} cm^{-3}, while varying the ratio between ZnS thickness and absorber layer CZTS one's (W_{ZnS}/W_{CZTS}), the total thickness of absorber and ZnS SP is kept constant to 700 nm.

We remark at figure 3 that the persence of ultra-thin ZnS SP layer between CdS and CZTS affect severly the performance of the solar cell where we noted a drop of V_{oc}, J_{sc} and FF which leads to the drop of efficiency by about 2%. Increase further the rotio W_{ZnS}/W_{CZTS} , the J_{sc} varies from 22.185 mA/cm^3 for W_{ZnS}/W_{CZTS}= 2% to 19.8 mA/cm^3 for W_{ZnS}/W_{CZTS}= 20% . That is a loss of 2.4 mA/cm^3, which is not negligible, corresponding to the loss in the absorption of the photons in the space charge region occurs in the ZnS layer due to the high band gap of this material (E_g=3.7 eV). Although increase of FF and V_{oc}, according to the thickness, the conversion efficiency drops drastically from 9.23 % to levels of 8.58%.

B. Modeling with various ZnS doping

Figure 4 shows open circuit voltage (V_{oc}), short circuit-current density (J_{sc}), fill factor (FF) and conversion efficiency (η) as a function of donor concentration ZnS secondary phase. All parameters increase slightly with doping ZnS concentration. This mainly can be explained by the reduction of the width space charge region in the ZnS second phase due to the augmentation of the carrier concentration. Which increases the number photons absorbed in the absorber layer.

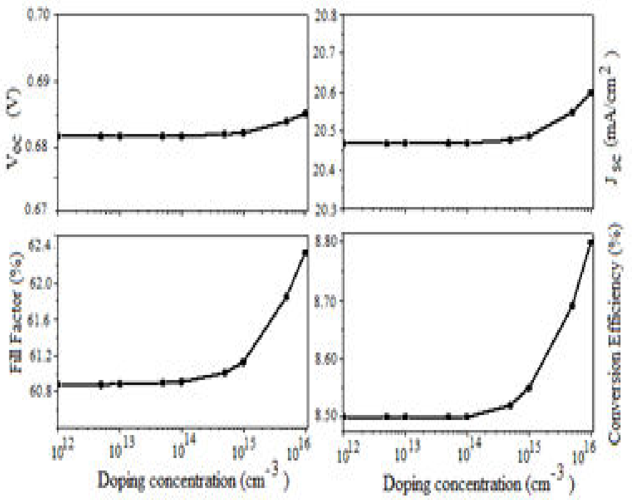

Fig.4 Dependence of (a) FF and η , (b) Jsc and Voc on the doping concentration of the second phase ZnS.

C. Material buffer layer effect

Generally, CZTS solar cell is used with CdS buffer, which has many advantages such as large band gap and the carrier density. Otherwise, the presence of Cadmium, a toxic material, is a disadvantage. To remedy the toxic CdS problem, the researchers try to replace the CdS by other buffer layers such as ZnS. In this section, as the second phase on the top of CZTS layer is ZnS we proposed to use the same type of material as a buffer layer. We try to compare the calculated results with those obtained with conventional CdS buffer layer.

In this simulation the thickness of buffer layer has been changed from 20nm to 100 nm and simulation result is illustrated in figure 5. It can be seen that, regardless of the material constituting the buffer layer, all cell parameters, except for fill factor, decrease with increasing thickness buffer layer. For both CdS and ZnS buffer layer, the drop of parameters is more pronounced for CdS at the presence of secondary phase.

It shows that the thickness increase of both CdS and ZnS as buffer layer, from 20 nm to 100 nm decreases the efficiency of the cell in CdS as buffer layer by about 0.7 %, however for ZnS as buffer layer the efficiency drop by about 0.22 %, which is due to reduced transmission of light to the absorber caused by the lower band gap of CdS compared to the ZnS ones. We noted a diminution of about 1.6 mA/cm^2 for CdS versus only 0.8 mA/cm^2 for ZnS ones.

However, the ZnS as buffer layer has shown the best performance than the CdS ones, we note an augmentation of efficiency from 0.86% to 1.16 % when we pass the CdS buffer layer to the ZnS one. So ZnS could be an alternative buffer to the CdS in the production of CZTS solar cells.

Fig.5 Dependence of FF, η, J_{sc} and V_{oc} on the thickness of buffer layer

IV. CONCLUSIONS

In the present work, the effect of the secondary phase ZnS, present on the top of CZTS layer, on the performance of solar cell is investigated numerically by using one dimensional SCAPS-1D computer software. The results demonstrate that ZnS second phase decreases the V_{oc}, J_{sc}, FF and η of solar cells. The high carriers' concentration ZnS secondary phase, enhance slightly the all performance solar cells, indicating a very little dependence on the doping concentration.

We have shown that the impact of the secondary phase ZnS deteriorate the device efficiency from 11% to levels of 8.58% depending on the thickness of ZnS SP. Independently to the material constituting the buffer layer, the efficiency decreases sharply, especially for CdS buffer layer. In the presence of de secondary phase ZnS on the top of CZTS the ZnS as buffer layer has shown the best performance than the CdS ones. ZnS could be an alternative buffer to the CdS in the production of CZTS solar cells.

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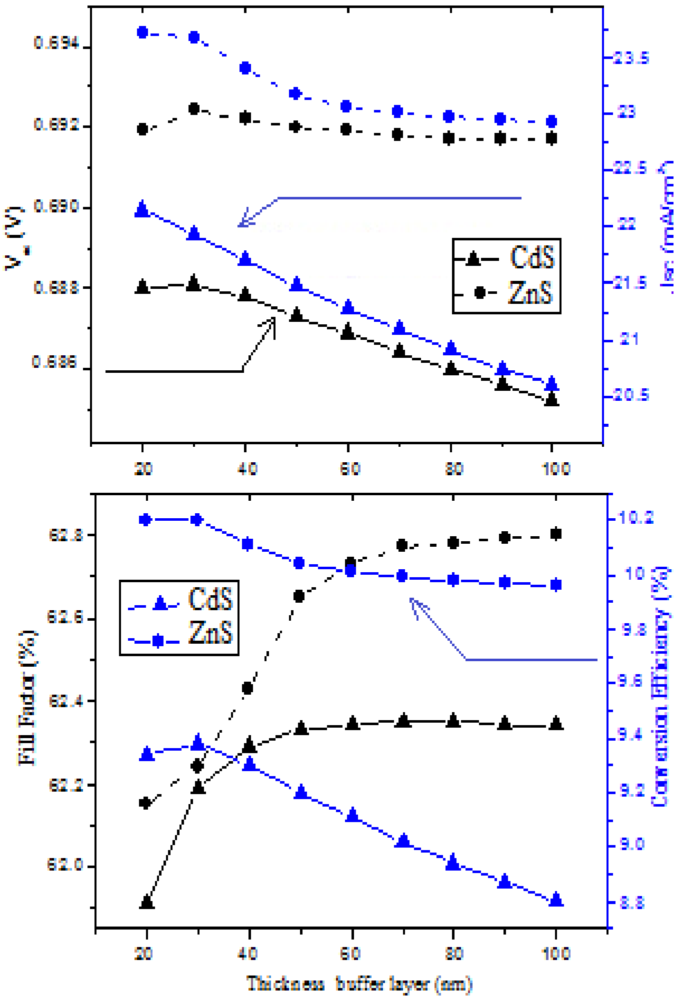

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