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The effect of copper concentration on CdS/CZTS heterojunction properties

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***Abstract*— Cu_2ZnSnS_4 (CZTS) / CdS heterojunctions have been prepared by a successive deposition of CZTS and CdS thin films on glass substrates by spray pyrolysis and chemical bath deposition techniques respectively. The concentration of cupric chloride in the starting solution has been varied in order to investigate its influence on device properties. The realized CZTS/CdS heterojunctions were characterized by recording their IV characteristics at ambient and at different temperatures. The current-voltage (IV) characteristics of the different heterostructures exhibit a rectifying behavior with a good ideality factor ranged from 1.5 to 2.7. From these IV characteristics we have deduced the saturation current series resistance and barrier height of the devices. We found that these quantities vary from 0.22 to 1.68µA for the saturation current and from 300 to 2500 Ω for the series resistance. We have deduced also that the potential barrier was found between 0.3 and 1.31eV. From these results we inferred that the realized structures are suitable for their applications as solar cells.**

***Keywords*— CZTS; heterojunction; spray pyrolysis; solar cells;IV**

I. INTRODUCTION

An ideal thin-film solar cell absorber material should have a direct band gap around 1.3–1.5 eV with abundant, inexpensive, and nontoxic elements. $Cu(In,Ga)Se_2$ (CIGS) is one of the most promising thin-film solar cell materials, demonstrating an efficiency of about 20% [1]. However, In and Ga are expensive components, and the band gap is usually not optimal for high efficiency CIGS solar cells. Currently, designing and synthesizing novel, high-efficiency, and low cost solar cell absorbers to replace CIGS has attracted much attention. Among the materials that have been investigated, quaternary Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) . CZTS has become the subject of intense interest because it is an ideal candidate absorber material for thin-film solar cells with an optimal band gap 1.5 eV, high absorption coefficient ($>10^4$ cm^{-1}), abundant elemental components, and is adaptable to various growth techniques [2–9] .The energy conversion efficiency of CZTS based solar cells has increased from 0.66% in 1996 to close to 7% recently [8]; however, it is still well below the Shockley –Queisser limit 32% [10].

The present work deals with electrical properties of CZTS/CdS heterojunction deposited by spray pyrolysis and chemical bath systems. Series resistance, saturation and ideality factor of the device are deduced from I-V characteristics.

II. EXPERIMENTAL

CZTS films used in this work were prepared by using spray pyrolysis method. Aqueous solution containing $CuCl_2.2H_2O$ as source of Cu, $Zn(C_2H_3O_2)_2.2H_2O$ as source of Zn, ,(0.005M) $SnCl_2.2H_2O$ as source of tin and (0.04M) $SC(NH_2)_2$ as sulfur source, were used in order to vary the Cu content in films the molarity of Cu salt was varied three values were used 0.005, 0.01 and 0.015M. Excess $SC(NH_2)_2$ is required to prevent oxidation and S deficiency in CZTS film through the spray deposition. Aqueous solutions containing precursor elements were sprayed onto glass substrate heated at temperature of 280°C , the solution feeding rate was fixed at 10ml/h and the deposition time is 45min. Cadmium sulfide (CdS) was used as an n-type layer, which was synthesized using chemical bath deposition. The thicknesses of CdS and FTO were around 90 nm, 100 nm respectively.

Finally a small golden dots of 2cm^2 were deposited onto absorber layer by DC sputtering system. I-V, characteristics of the realized devices were achieved by using Tektronix 370 curve tracer to visualize and recorder IV curves. The IV measurements were carried at different temperature from the ambient to 100 ºC.

III. RESULTS AND DISCUSSION

Characteristic I-V is the principle characteristic of the heterojunction. The exploitation of this characteristic leads to certain parameters such as the saturation current, series resistance and the ideality factor. The electrical measurements were carried in dark at different temperatures.

The performed I-V measurements as a function of

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temperature are shown in Fig. 1. With increasing temperature the s-shape straightens out pointing towards a thermionic emission barrier [11].Fig.2, shows the I-V characteristics of different CZTS/CdS heterojunctions prepared with various Cu salt concentration in the solution. CZTS films were obtained by the dissolved solutions of zinc acetate (0.005M) and cupric chloride (0.005,0.010,0.015M), in water distilled. As one can see, the obtained characteristics have a rectifying behavior indicating that the structure carried out is a well heterojunction

The series resistance Rs of solar cell is important parameter that mainly affects the solar cells performances such as open circuit voltage and efficiency. Series resistance is the sum of resistances due to all components present in the path of the current. In order to identify this issue, we studied the temperature dependence of the I–V plots in dark conditions,Fig. 3.Using the congruent method

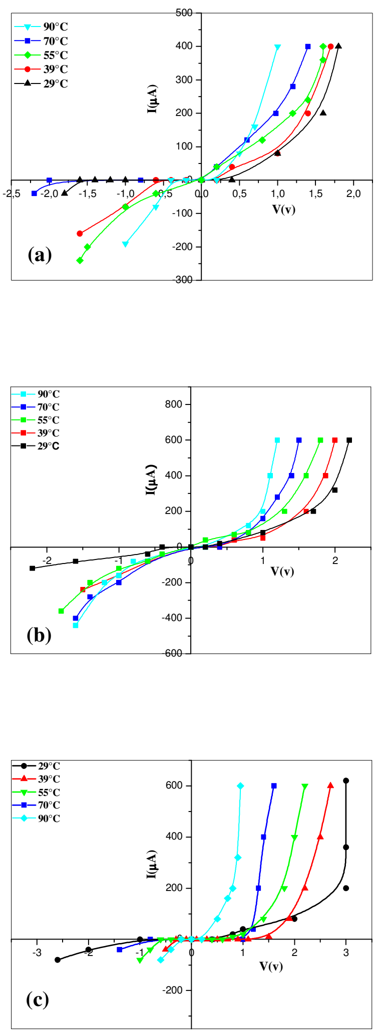

Fig. 1 Caracteristic I-V of the CZTS/CdS heterojunction variation as a function of temperature and different salt concentration: cupric chloride case (a):0.005,(b):0.010M, (c):0.015M

TABLE I

Variation of the saturation current, ideality factor and potential barrier as a function of different salt concentration: cupric chloride case.

Cu salt Molarity	I_s (μA)	n	Ea (eV)	Rs (Ω)
0.005M	1.05	1.50	0.34	60
0.010M	0.61	1.80	0.54	140
0.015M	0.22	2.70	1.31	560

described in the previous studies [12] ,to extract dark series resistance R_S .from diode I–V equations and to estimate the barrier height(Φ) (TABLE I).

The ideality factor (n) of a diode indicates how closely the diode follows the ideal diode equation. The forward current in p-n junction is dominated by diffusion of minority carriers injected into the neutral regions of the junction. This type of current yields to an ideality factor of 1. Recombination of carriers in the space charge region, mediated by recombination centers located near the intrinsic Fermi level, results in an ideality factor of 2 [13].

Value of *n* can be estimated directly from the current-voltage I-V data by calculating the slopes of the straight-line regions of dark Log *I* vs. *V*, from the result shown in (TaABLE I) it can be seen that the ideality factor is varied between 1.5 and 2.7.

Fig.4, shows the variation of the saturation current as a function of temperature and different salt concentration of the cupric chloride (0.005,0.010, 0.015M). The saturation current is varied between 0.22 to 1.68µA.

The activation energy of saturation current is equal to ΔEc discontinuity between the conduction band of CZTS and CdS in the case of device prepared with a salt copper molarity equal to 0.005M and 0.010M. However, in the case of copper molarity fixed at 0.015 M, the saturation activation energy is equal to 1.31 eV which is same of the defect level in he CZTS band gap deduce from photoluminescence measurements [14] .

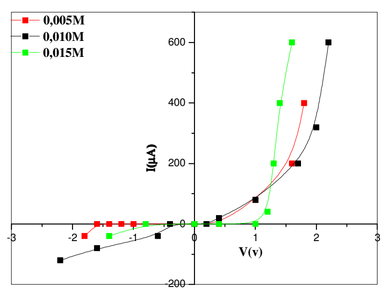

Fig. 2 I-V Characteristic of the CZTS/CdS heterojunction variation as a different salt concentration: cupric chloride case.

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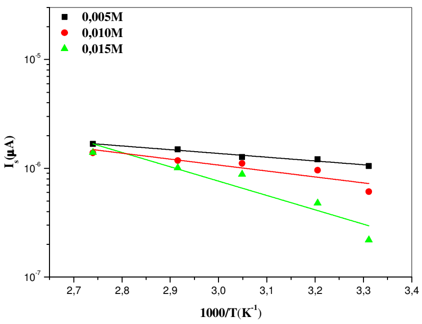

Fig. 3 Variation of the series resistance as a function of temperature and different salt concentration: cupric chloride case.

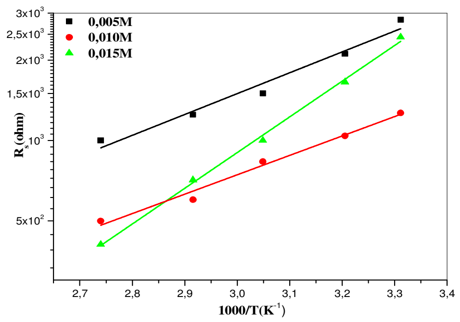

Fig.4 Variation of the saturation current as a function of temperature and different salt concentration: cupric chloride case.

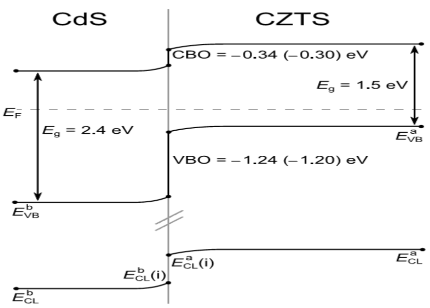

Fig. 5 Band diagram of the CdS/CZTS interface resulting from this work. The values of the CBO and VBO reported in parentheses are obtained by the indirect method [15].

Knowing the 1.5 and 2.4 eV for the CZTS and CdS band gaps respectively, the CBO calculated with the indirect method results to be (−0.30 ± 0.14) eV, while the CBO resulting from VB analysis is (−0.34 ± 0.06) eV. A schematic band diagram of the CdS/CZTS interface with the values measured in this work is shown in Fig. 5, and could be one of the reasons for the Voc limitation usually reported for the actual CZTS solar cell technology. In order to improve the device performances, further efforts have to be addressed to engineer new buffer layers with optimized band alignment with CZTS absorber, thus reducing interfacial recombination phenomena [15].

V. CONCLUSIONS

CZTS/CdS heterojunctions could be successfully deposited by spray pyrolysis technique. For different concentrations solutions of the cupric chloride (0.005, 0.01,0.015 mol/l) and zinc acetate (0.005M) dissolved in water distilled .The I-V characteristics measurement temperature was varied between 29 and 90 °C. According to the result of characteristic I-V, the saturation current variation is ranged from 0.22 to 1.68µA, series resistance from 300 to 2500Ω and ideality factor from 1.5 to 2.7 respectively.

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