Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1493 - 1498

PREPARATION AND CHARACTERIZATION OF THE JUNCTION n-$CuInSe_2$/p-CdTe SOLAR CELL BY THE STACKED ELEMENTAL LAYER (SEL) TECHNIQUE

A. Ashour[*], A. A.Ramadan[a], K. Abd EL-Hady, A. A. S. Akl

Physics Department, Faculty of Science, Minia University, Minia, Egypt
[a]Physics Department, Faculty of Science, Helwan University, Helwan, Cairo, Egypt

$CuInSe_2$/CdTe heterojunctions were prepared by stacking elemental layers (SEL) of Cu, In and Se onto p-CdTe single crystals in vacuum and followed by annealing at 300 ^oC in air for heating time $\geq$ 1h. Heterojunction solar cells were fabricated using the configuration Au/$CuInSe_2$/CdTe/Al. The electrical properties of the $CuInSe_2$/CdTe heterojunctions were studied by means of current-voltage (I-V) measurements carried out at different temperatures. The dark I-V characteristics show that a recombination mechanism controls the transport of charge carriers across the junction. On illumination, appreciable change in the I-V characteristics and photovoltaic effects were observed. Open circuit voltage (V_{OC}) of 285 mV, short circuit current density (J_{SC}) of 41 mA cm^{-2}. The solar energy conversion efficiency gave a value of about 4.2% without any attempt at optimisation of the cell parameters were produced by the cells.

(Received February 2, 2005; accepted May 26, 2005)

Keywords: Heterojunction, $CuInSe_2$/CdTe, SEL Technique, I-V Characteristics, Illumination

1. Introduction

Heterojunction solar cells have the potential to achieve the goals of higher efficiency, reliability and low cost, necessary for the large scale applications. For solar cell applications and photo-detector, other semiconductors than silicon, which have an energy gap between 1.1 and 1.6 eV, are preferred to obtain optimum efficiencies. Several studies [1] on heterojunction using CdS have been made for photovoltaic application during the last decade. $CuInSe_2$/CdS heterojunction is the widely studied for solar cell applications because of its good lattice match and the absence of any interfacial spike in the conduction band [2]. On the other hand, CdTe is also important due to the wide range of its applications in photovoltaics and detectors [3]. Recently, heterojunctions based on CdTe like $CuInSe_2$/CdTe, have been studied.

$CuInSe_2$ is a direct band-gap semiconductor (1.04 eV) belonging to the I-III-VI_2 group of semiconductors with the chalcopyrite structure. Different techniques to fabricate $CuInSe_2$ thin film absorbers as flash evaporation [4], spray pyrolysis [5], sputtering [6] and stacking elemental layer [7]. The stacked elemental layer (SEL) is a technique suitable for large area development because of the simplicity of control of deposition parameters and the flexibility in the choice of processing method of the elemental stacks into $CuInSe_2$.

In this paper, heterojunctions of $CuInSe_2$/CdTe have been fabricated by depositing $CuInSe_2$ thin films with stacked elemental layer (SEL) technique on p-type CdTe single crystals. The electronic properties of the fabricated $CuInSe_2$/CdTe heterojunction solar cells were analysed.

2. Experimental details

The CdTe substrates with a surface area of about 1 cm^2 were prepared from slices 0.1 cm thick obtained from crystalline ingots grown by the Bridgman method [8]. The crystals were p-type not doped and showed holes density ranging from 10^{17} to 10^{18} cm^{-3}. Heterojunctions have been

[*] Corresponding author: aashour_2000@yahoo.com

fabricated between films of $CuInSe_2$ prepared by elemental layer technique and single crystal of CdTe with the configuration Au/$CuInSe_2$/CdTe/Ag as shown in Fig. 1. Details of the SEL technique of the used $CuInSe_2$ films have been reported elsewhere [7]. Polished aluminium sheets were used as substrates for $CuInSe_2$/CdTe heterojunctions. The junctions were prepared by stacking elemental layer of the n-$CuInSe_2$ film of 1μm thickness onto polished p-type single crystal of CdTe at room temperature. The heterojunctions were then annealed at 350 ^{o}C for 1 hour. The front contact of $CuInSe_2$/CdTe cell was achieved with a grid of gold and the back one on p-CdTe single crystal was obtained by stick it with the aluminium substrate by silver paste. The ohmic contact nature for Al/CdTe and Au/$CuInSe_2$ was tested separately prior to the factorization of the heterostructure.

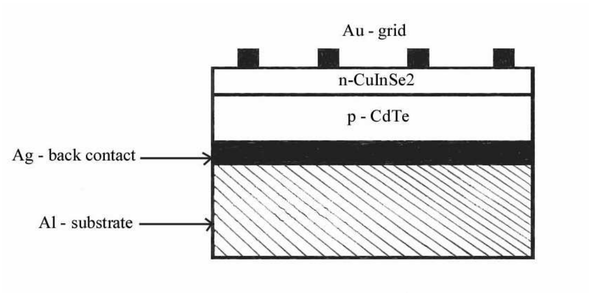

Fig. 1. Schematic diagram of a cross-section of n-$CuInSe_2$/p-CdTe solar cell.

The junction characteristics were analyzed in terms of current-voltage (I-V) measurements. The I-V characteristics in dark and under 100 mW cm^{-2} illumination by using a halogen lamp on $CuInSe_2$ side through the transparent grid of gold contact. The temperature variation (263 – 323 K) on the I-V characteristics was studied under the dark condition. The cell parameters V_{OC}, I_{SC}, FF, and also the conservation efficiency were calculated.

3. Results and discussion

The I – V characteristics of $CuInSe_2$/CdTe heterojunctions (HJ) under investigation in dark condition at different temperatures are shown in Fig. 2. The heterojunction had good rectification properties considerable change was observed in the reverse bias. It shows that, the I – V characteristics in the forward direction differ markedly from those in the reverse direction. At a certain voltage, the current increases with increasing temperature in both the forward and reverse direction. Since the dark I – V plots were similar to the diode characteristics. The current – voltage relation in heterojunction can be generally described by any of the diffusion model, the emission model or the recombination model [9] from which the relation is represented by the standard diode equation [10]:

$$J_f = J_o \{ \exp (eV/nkT) -1\} \quad (1)$$

where e is the electronic charge, n is the diode quality factor, k is Boltzmann's constant, T is the absolute temperature and Jo is the reverse saturation current density.

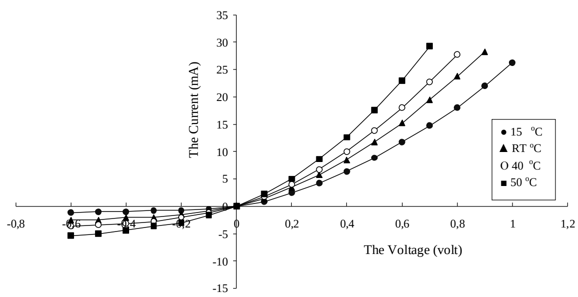

Fig. 2. I – V characteristics of $CuInSe_2$/CdTe heterojunction in dark condition at different temperatures.

The semi-log plot of forward I – V characteristics of the heterojunction is shown in Fig. 3. The saturation current density was obtained by extrapolating the J – V characteristics at low voltage, where the values were found to be in the ranges from 10^{-7} to 10^{-6} A cm^{-2}. It is to be noted that the diode factor, n, could be calculated from the slope of certain voltage interval. The values of n were found to vary from 2.3 to 2.5 at the temperature range from 15 to 50 ^{o}C respectively. The increase in n values (> 2 ideal value) indicates that the cells were non-ideal and most of the carriers (electrons and holes) were recombined at the junction (depletion) region [11-13]. Hence, as the voltage increases, the current is limited by the carrier recombination. This could be due to the lattice mismatch of the $CuInSe_2$/CdTe system, which may give rise to a large number of interface states [4].

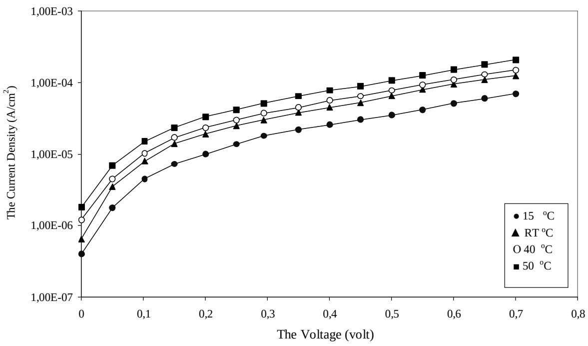

Fig. 3. Semilogarithmic relation of current voltage characteristic of $CuInSe_2$/CdTe heterojunction cell in dark condition at different temperatures.

Analysis of the temperature dependence of I – V curves at constant voltage, yields the following relation [14]:

$$J_o = J_{oo} \exp\left(-\Delta E/kT\right) \qquad (2)$$

where J_{oo} is the constant determined by the particular type of the junction and ΔE is the activation energy. According to this equation, J_o should change exponentially with temperature. On the other hand, the pre-exponential factor, J_o, which obtained by extrapolating the forward current curves shown in Fig. 3 to zero voltage is found to vary exponentially with 1/T as shown in Fig. 4. Therefore, plotting $\ln J_o$ vs. 1/T yields a straight line, where the activation energy of the charge carriers, ΔE, can be determined from the slop. It was found that the value of ΔE is equal to 0.38 eV. This suggests that the hole in the valence band of CdTe (p) flows from one localized state to another in $CuInSe_2$ (n) located within an energy range of kT by a multi-step tunneling process, and it keeps flowing near the edge of the depletion region of $CuInSe_2$ where the tunneling rate decreases due to a decrease of the electric field. This hole is then recombined within an electron in the conduction band of $CuInSe_2$ or it is emitted to the valence band of $CuInSe_2$ [15]. The temperature dependence in equation 2 arises from either the recombination or emission process of the tunneling hole [16].

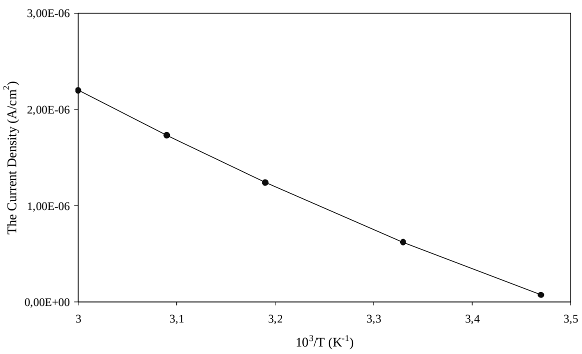

Fig. 4. The current density versus 1/T of $CuInSe_2$/CdTe heterojunction solar cell in dark condition.

The values of the series resistance (R_S) in dark condition for the cell can be determined from the forward J-V characteristics of Fig. 3 at higher voltage. Thus, for a given current density, J, at a certain temperature, the linear part gives the voltage drop, $\Delta V = JR_S$, across the neutral region. The plot of ΔV versus J shown in Fig. 5 should give a straight line whose slope yields the value of the series resistance. The results given are R_S from 19 to 28 kΩ at temperature from 15 to 50 ^{o}C respectively. As we seen, by increasing the temperature, the series resistance increased and the current density of the cell decreased. The higher resistivity may be responsible for decreasing the quality of the cell [17].

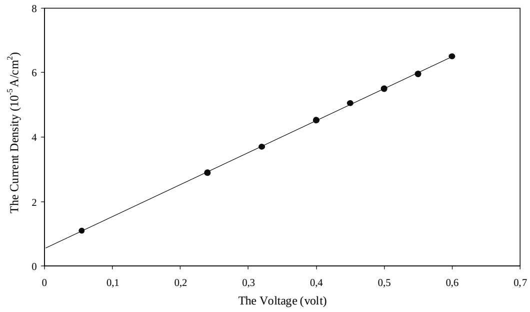

Fig. 5. Relation of current - voltage characteristic of $CuInSe_2$/CdTe solar cell due to the series resistance in dark condition.

Based on the Anderson [18] model for the heterojunction, a theoretical energy-band diagram for p-$CuInSe_2$/n-CdTe heterojunction was constructed as shown in Fig. 6. The space charges considered here are referred to as depletion regions in which the free carriers are swept out by the electric field. Since the work function of CdTe (4.40 eV) was less compared to that of $CuInSe_2$ (5.39 eV), the band bending at the junction will be as shown in Fig. 6. Also, the space charge layers in the two semiconductors have widths denoted by W_n and W_p respectively. The shape of the band edges relative to a constant energy line is determined by Poisson's equation in all cases. The form of this equation indicates that a positive charge distribution results in bands, which are bent upward, and oppositely for a negative space charge distribution. Also, the rate of charge of the slope is directly proportional to the charge density. Thus, the space charge results in the diffusion potentials denoted by V_n and V_p. An additional source of charge is that due to ionized interface states. This results in a planer charge distribution, which for interfaces between poorly lattice matched materials can have values comparable to the total charge per unit area is the depletion regions [19]. As such, it must be considered in determining the shape of the bands. Qualitatively, the effect of the interface charge is similar to that of the space charge, only confined to a single plane. Instead of concavities there are kinks in the bands at the interface due to the interface charge. The interface charge density may depend on the location of the Fermi levels.

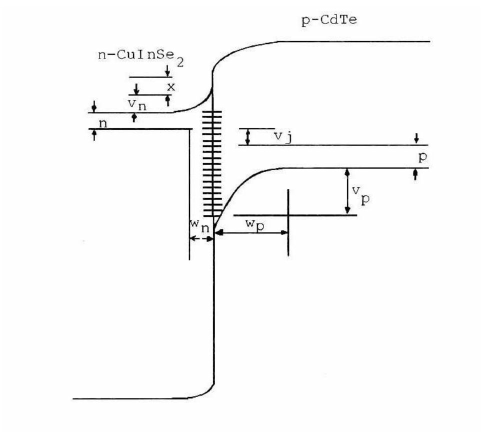

Fig. 6. Energy band diagrams of $CuInSe_2$/CdTe solar cell.

$CuInSe_2$/CdTe heterojunction was tested under illumination, without any attempt to optimize the solar cell performances. The cell was equipped with a grid gold contact and the junction was illuminated through the grid. Fig. 7 shows the J-V characteristics under illumination. The open-circuit voltage (V_{OC}) is 285 mV while the short circuit current density (J_{SC}) is 41 $mAcm^{-2}$. The photovoltaic response shows a poor fill factor (FF) of 0.46. Since the light power density was 100 $mWcm^{-2}$, we can estimate a solar efficiency of about 4.2%. It should be noted that the quoted η values refers to an engineering efficiency and that no corrections were made for reflected or transmitted lights. However, these values are fairly good compared with previously reported values for cells incorporating semiconductor heterojunction devices [12]. Nevertheless, further improvement of the cells is necessary to meet the requirements for practical use. The main limitations of the photovoltaic response appear to be the low cell parameters (fill factor, open-circuit voltage, short circuit current and efficiency). The important factor in lowering these parameters is the presence of series resistance effects as we mentioned before. The series resistance of the n-$CuInSe_2$/p-CdTe cell as measured from J-V characteristics was in the range 19-28 kΩ. These values are mainly due to the resistance of $CuInSe_2$ and CdTe substrates.

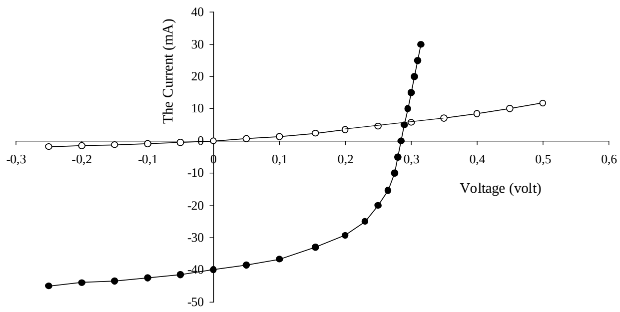

Fig. 7. I – V characteristic of CuInSe2/CdTe solar cell in dark and illumination at room temperature.

On the other hand, we can introduce the relation between V_{OC} and J_o as [12]:

$$V_{OC} = [nkT / e] \ln(J_{SC}/J_o) \quad (3)$$

From this equation, the primary loss in V_{OC} is due to the high value of J_o. The high value of J_o can be attributed to the presence of interface states. Furthermore, the high values of J_o will reduce the fill factor. The interface states are due primarily to the lattice mismatch between the pair of semiconductors ($CuInSe_2$, CdTe), but they are strictly related also to the substrate preparation procedure and to the formation process [20, 21]. However, further investigations are necessary to determine the influence of the preparation parameters on the junction properties.

4. Conclusions

Heterojunction devices of $CuInSe_2$ onto p-CdTe substrate have been fabricated by stacking elemental layer (SEL) method. The junctions have been characterized using different measurements in dark and illumination. The junctions exhibit rectifying characteristics showing a p-n diode-like behaviour. The current – voltage measurements suggest that the forward current in these junctions involves recombination mechanism. The series resistance and the activation energy of the charge carriers have been obtained by analyzing the dark current – voltage characterizations. An energy band diagram is proposed. The cell parameters under illumination were calculated. Further improvements can be expected from an investigation of the influence of the preparation parameters on the junction properties.

References

[1] L. L. Kazamerski, F. R. White, M. S. Ayyagiri, Y. T. Juanig, R. P. Patterson, J. Vac. Sci. Technol. **14**, 65 (1977).
[2] Y. Kokubun, M. Wada, Jpn. J. Appl. Phys. **16**, 879 (1977).
[3] J. Sarie, Shin-Ichi Yama Giwa, H. Matsunem, T. Taneka, Solid State Electron. **24**, 845 (1981).
[4] J. J. B. Prasad, D. Krishna Rao, J. Sobhanadri, J. Appl. Phys. **59**, 2866 (1985).
[5] S. Duchemin, J. Bougnot, A El. Ghzizal, K. Belghit, International Conference on Applications of Solar and Renewable Energy, March 19-22, 1989. Cairo (Egypt).
[6] N. Romeo, A. Bosio, V. Canevari, Proceedings of the Euroforum-New Energies Congress V. 3, 24-28 October 1988, Saarbrücken (Germany).
[7] A. Ashour, A. A. S. Akl, A. A. Ramadan, K. Abd EL-Hady, Thin Solid Films **467**, 300 (2004).
[8] S. Yamada, Jpn. J. Appl. Phys. **15**, 1940 (1960).
[9] S. M. Sze, Physics of Semiconductors Devices, 2nd edn. Wiley Inter-Science, New York, 1981.
[10] S. M. Sze, in: Physics of Semiconductor Devices (Wiley, New York, 1981).
[11] J. J. B. Prasad, D. Krishna Rao, J. Sobhanadri, J. Appl. Phys. **59**, 2866 (1986).
[12] D. Y. Song, J. Zhao, A. Wang, P. Widenborg, W. Chin, A. G. Aberle, Proc. 17th European Photovoltaic Solar Energy Conference, (WIP, Munich, 2001), p. 1865.
[13] S. Darwish, H. S. Soliman, A. S. Riad, Thin Solid Films **259**, 248 (1995).
[14] S. K. Das, G. C. Morris, Solar Energy Materials, Solar Cells **28**, 305 (1993).
[15] K. Aguir et al., Thin Solid Films **257**, 98 (1995).
[16] H. Matsuura, J. Appl. Phys. **55**, 1012 (1984).
[17] F. O. Adurodija, M. J. Carter, "Fabrication and Characterisation of $CuInSe_2$ Thin Film Solar Cells By Stacked Elemental Layer (SEL) Technique", Newcastle Photovoltaic Application Centre, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK.
[18] R. L. Anderson, Solid State Electron. **5**, 341 (1962).
[19] U. Kaufmann and J. Schnneider, "Ternary Semiconductors Type I-III-VI and II-IV-V" In Festkorper probleme XIV (1974).
[20] A. M. Mancini, P. Pierini, A. Valentini, L. Vasanelli, Thin Solid Films **124**, 85 (1985).
[21] A. A. Ibrahim, "Fabrication and Characterization of ZnO/Si Heterojunction Solar Cell Prepared By Thermal Evaporation Technique", introduced to the 8th International conference on Solar Energy and Applied Photochemistry, 20-25 February 2005, Luxor, Egypt, and also to be published in Turk. J. of Physics (2005).