THIN FILM SOLAR CELLS ON THE BASE OF $p-CuInSe_2/Cd_{1-x}Zn_xS_{1-y}Se_y$ ELECTRODEPOSITED HETEROJUNCTION

A.Sh.Abdinov, H.M.Mamedov, and S.I.Amirova

Department of Physical Electronics, Faculty of Physics, Baku State University, 370148, Z.Khalilov str., 23, Baku, Azerbaijan, tel: 99412-39-73-73, e-mail: mhhuseyng@yahoo.co.uk

ABSTRACT

Detailed electrical and photoelectrical measurements are carried out on $Mo/CuInSe_2/Cd_{1-x}Zn_xS_{1-y}Se_y$ thin solar cells prepared by electrochemical deposition. It was found that annealing the heterojunctions at 120÷150°C for 6÷7 min in air leads to an improving of the electric and photoelectric parameters. The open circuit photovoltage and short circuit photocurrent density of cells $Mo/CuInSe_2/Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$ under illumination intensity of 100 mW/cm^2 from a W-halogen lamp were V_{oc} = 0.58 V, J_{sc} = 18 mA/cm^2, respectively.

Keywords: film, solar cell, heterojunction, photovoltage, photocurrent.

I. INTRODUCTION

Intensive efforts have been made to improve the parameters of solar cells based on wide-gap $A^{II}B^{VI}$ materials, e.g., $CuInSe_2/A^{II}B^{VI}$ [1 – 5]. The quality and efficiency of the solar cells based on the substrate material is limited by structural defects due to the structural imperfection in the substrate and lattice mismatch stress. Among the $A^{II}B^{VI}$ family, $Cd_{1-x}Zn_xS$ was originally chosen for its lattice match to $CuInSe_2$ substrates and thin film cells based on these materials have been reported to show an efficiency of 14-16%. Its shown in this paper that the efficiency of $CuInSe_2/Cd_{1-x}Zn_xS$ solar cells maybe improved by addition of selenium to $Cd_{1-x}Zn_xS$ films.

Metal chalcogenide thin films preparations by electrochemical method are currently attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. However, growth of $Cd_{1-x}Zn_xS_{1-y}Se_y$ films by electrodeposition onto the *Mo/CuInSe$_2$* substrates has not been reported by now.

In this paper, we prepared $Mo/CuInSe_2/Cd_{1-x}Zn_xS_{1-y}Se_y$ heterojunction (HJ) solar cells by electrodeposition method and investigated the effect of the film composition x, y and heat treatment conditions on the electrical and photoelectrical properties of these HJ.

II. EXPERIMENTAL

Electrodeposition of the $CuInSe_2$ films onto the Mo substrates was carried out at room temperature from aqueous solution containing 50 mM each of $InCl_3$, SeO_2 and $CuCl$. The deposition potential was –0.76 V and the current density was 8 to 11 mA/cm^2. The thickness of the films were 2 ÷ 3 μm. The as-deposited films were black in colour, very smooth and uniform. The resistivity of the films were ρ = 12 ÷ 30 Ohm·cm.

Thin films of $Cd_{1-x}Zn_xS_{1-y}Se_y$ (CZSSE) in the composition range $0.1 \le x \le 0.8$ and $0 \le y \le 0.2$ were deposited at room temperature on $Mo/CuInSe_2$ substrates from an aqueous solution containing cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$), sodium thiosulfate ($Na_2S_2O_3$) and sodium selenosulfate ($Na_2Se_2O_3$) or selenium oxide (SeO_2). The distance between vertically suspended electrodes was 2 ÷ 3 cm. Deposition was carried out for 30 min at potentials of – 0.7 to – 0.85 V and current densities of 12 to 18 mA/cm^2, respectively for the various values of x and y. The composition of the mixed films altered with the concentration of Zn and Se. The as-deposited films are well adhesive to the substrate, 7 to 8 μm thick. All the films, as prepared and annealed, show n-type conductivity. As ohmic contacts we used In or Ag. Ohmage of contacts was controlled by current-voltage characteristics (*I-V*). The active area of HJ was 0.5 ÷ 4 cm^2.

III. RESULTS AND DISCUSSION

The dark current-voltage (*I-V*) characteristics of the as prepared heterojunctions depending on the film composition, x and y, are shown in figure 1. Studies of *I-V* characteristics showed that the as prepared HJ $CuInSe_2/Cd_{0.6}Zn_{0.4}S_{0.9}Se_{0.1}$ were rectifying k = 180 at 1 V (Figure 1, curve 1), decrease, when zinc concentration x

increases, with the direction always corresponding to an external negative bias on CZSSE films.

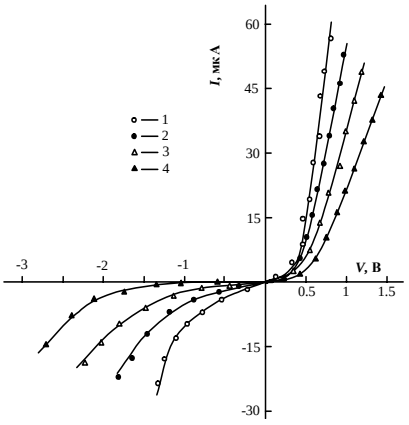

Fig. 1. Dark I-V characteristics of the as deposited $CuInSe_2 / Cd_{1-x}Zn_xS_{1-y}Se_y$ heterojunctions at 300 K. x : 1 – 0.4; 2 – 0.5; 3 – 0.6; 4 – 0.7. y : 1 – 0.1; 2 – 0.1; 3 – 0.2; 4 – 0.2.

Figure 2 shows the effect of heat treatment condition on the current-voltage characteristics of the HJ $Mo/CuInSe_2/Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$.

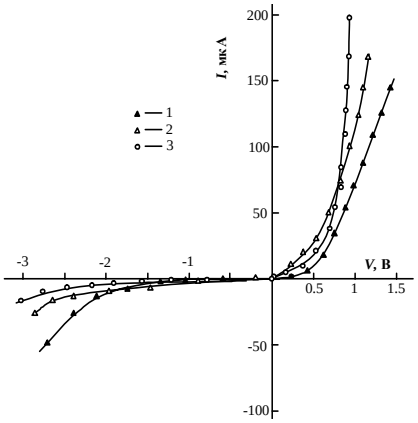

Fig. 2. Dark *I-V* characteristics of the annealed $CuInSe_2 / Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$ heterojunctions at 300 K: T_a, °C: 1 – 0; 2 – 100; 3 – 150; τ_a, min: 1 – 0; 2 – 3; 3 – 6

The series resistance of the HJ was decreased, with increasing the annealing temperature from 0 to 150°C (τ_a = 6 min). The estimate of the series resistance was made in the high current region of the *I-V* curves, which is typically dominated by series resistance. Best rectification for annealed HJ is about k = 2000 (Figure 2, curve 3).

The forward *I-V* characteristics of annealed HJ in a $\lg I = f(U)$ plot are straight lines, which is indicate of the exponential dependence of current on voltage up to the cut-off voltage (V_d). The analysis of the *I-V* characteristics with different models of current passage shows that the passage of current through the heterojunctions is due to tunnel-recombination model by Riben and Feucht in the case of multiple step tunnel recombination processes [6]. With increasing forward bias $V \geq 0.5 \div 1$ V, a linear approximation of the *I-V* characteristics gives value V_d = 0.6 V for HJ with x = 0.7 and y = 0.2.

The reverse current of the HJ obeys a linear law at relatively low (V = 0.5 ÷ 1 V) and exponential law at high voltages.

Figure 3 shows the light current-voltage characteristics of the annealed HJ versus the film composition x and y, at AM 1.5 conditions. It can be clearly seen that the conversion efficiency of HJ with increasing y from 0 to 0.2 was increased.

The highest open circuit photovoltage and short circuit photocurrent values for the HJ $Mo/CuInSe_2/Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$ were V_{oc} = 0.58 V, J_{sc} = 18 mA/cm^2, respectively (Figure 3, curve 3).

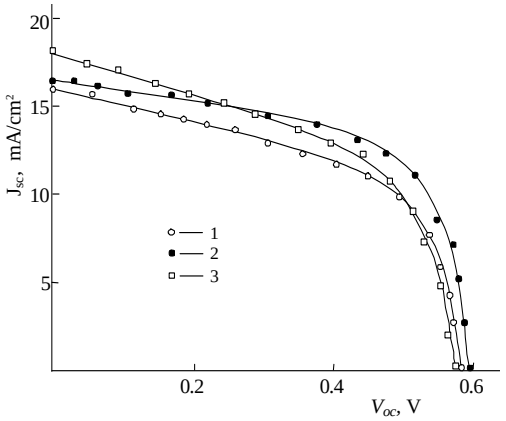

Figure Fig.3. *I-V* characteristics of the annealed $CuInSe_2 / Cd_{1-x}Zn_xS_{1-y}Se_y$ heterojunctions at 300 K: x : 1 – 0.7; 2 – 0.7; 3 – 0.7; y : 1 – 0; 2 – 0.1; 3 – 0.2

The voltage-capacitance characteristics revealed the annealed in air at 150°C for $\tau_a = 6 \div 7$ min HJ to be sharp. From the plot of figure find V_d = 0.61 V for heterojunctions with x = 0.7 and y = 0.2.

Additional information on the effect of annealing temperature and time on the parameters of the heterojunctions could be obtained by investigating the influence of annealing condition on the photoelectric properties of the heterojunctions.

Figure 4 shows the room temperature photosensitivity spectrum of the $Mo/CuInSe_2/Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$ heterojunctions annealed at various temperatures.

As the annealing temperature was increased from 0 to 100°C (τ_a = 3 min), the intensity of peak in the λ_{m1} = 0.560 μm wavelength region sharply increases (Figure 5, curve 2). Upon heat treatment in air at T_a = 150°C for τ_a = 6 min, the HJ exhibit high photosensitivity over a wide spectral range (Figure 5, curve 3). Figure 5 also shows that the photosensitivity is decreased, when the annealing temperature is increased from 150 to 200°C (τ_a = 9 min).

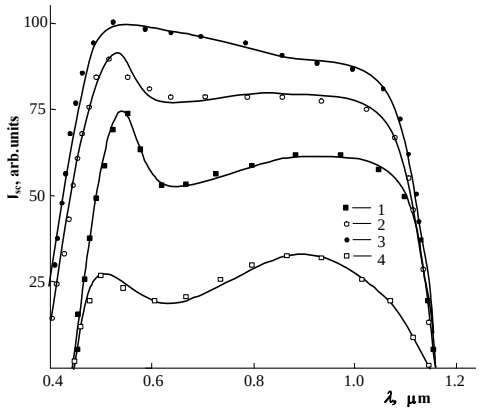

Fig.4. Short circuit photocurrent spectrum of $CuInSe_2$ / $Cd_{0.3}Zn_{0.7}S_{0.8}Se_{0.2}$ heterojunction as a function of annealing condition:
T_a, °C: 1 – 0; 2 – 100; 3 – 150; 4 – 200
τ_a, min: 1 – 0; 2 – 3; 3 – 6; 4 - 9

The changes of the heterojunction parameters with heat treatment condition are explained on the basis of electronic-molecular interaction of film surface with the oxygen [7].

IV. CONCLUSION

Anisotype $Mo/CuInSe_2/Cd_{1-x}Zn_xS_{1-y}Se_y$ heterojunctions are prepared by the electrodeposition method. Their base characteristics were studied depending on the composition of CZSSE films and annealing condition.

The improving in the electrical and photoelectrical properties of the HJ with increasing annealing temperature from 0 to 150°C is attributed to the electronic-molecular interaction of films surface with oxygen. It is established that HJ with $y = 0.2$ possess the high photosensitivity after the annealing in air at T_a = 150°C for τ_a = 6 min. Under the AM 1.5 condition the open circuit photovoltage and short circuit photocurrent density of best structures were V_{oc} = 0.58 V, J_{sc} = 18 mA/cm^2, respectively.

The parameters of a HJ did not show sign of any degradation processes over the 9 – 11 month.

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