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Electrical and photoelectrical properties of isotypic $In_2O_3/Cd_{1-x}Zn_xS/CdS_{1-y}Se_y$ heterostructures

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In_2O_3 / $Cd_{1-x}Zn_xS$ / $CdS_{1-y}Se_y$ heterostructures are prepared by the electrodeposition method. The dependence of the electric and photoelectric parameters of heterostructures on the composition of $Cd_{1-x}Zn_xS$ ($0 \le x \le 0.8$) and $CdS_{1-y}Se_y$ ($0.3 \le y \le 0.9$) films and heart treatment condition were investigated. It was found that annealing the heterojunctions In_2O_3 / $Cd_{0.4}Zn_{0.6}S$ / $CdS_{0.2}Se_{0.8}$ at T_a = 380 ÷ 400 °C for τ_a = 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 In_2O_3 / $Cd_{0.4}Zn_{0.6}S$ / $CdS_{0.2}Se_{0.8}$ at illumination 1500 lx and temperature 300 K were V_{oc} = 0.48 V, J_{sc} = 5.9 ÷ 6.3 mA/cm^2, respectively.

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1. Introduction

Ternary $Cd_{1-x}Zn_xS$ and $CdS_{1-y}Se_y$ are considered to be promising materials for solar cell applications because of their high optical absorption coefficient, as well as its versatile optical and electrical properties which can, in principle, be purposefully controlled by variation of its composition, heat-treatment temperature and time [1 – 5].

As is known, thin film solar cell technology offers the best hope for obtaining photovoltaic devices with low cost and reasonable efficiency. Electrodeposition method is a versatile technique, which is simple, economic and useful for large area deposition [6 – 11].

In the present paper, we report on the preparation of In_2O_3 / $Cd_{1-x}Zn_xS$ / $CdS_{1-y}Se_y$ heterostructures and show the influence of the films composition and heat treatment conditions on the electrical and photoelectrical properties of these heterojunctions.

2. Experimental details

In_2O_3 films with thickness 1 ÷ 2 μm have been prepared by magnetron sputtering from pure indium targets onto the cleaned surface of quartz substrates, which used as a cathode at deposition of the $Cd_{1-x}Zn_xS$ films. Electrodeposition of the $Cd_{1-x}Zn_xS$ films with several compositions in the range $0 \le x \le 0.8$, onto the In_2O_3 substrates was carried out at room temperature from aqueous solution containing cadmium ($CdCl_2$), zinc ($ZnCl_2$) and sodium ($Na_2S_2O_3$) salts. The distance between electrodes was 2 ÷ 3 cm. The deposition potential was controlled at a value between – 0.4 to – 2.5 V. The current density during the deposition was increased from 7.5 to 38 mA/cm^2, with the increase of negative deposition potential. The thickness of the films were 2 ÷ 8 μm. Polycrystalline $n-Cd_{1-x}Zn_xS$ films for various compositions had carrier concentration in the range $4\times10^{15} \div 7\times10^{16}$ cm^{-3} at 300 K.

Electrodeposition of the $CdS_{1-y}Se_y$ films in the composition range $0.3 \le y \le 0.9$, onto the $In_2O_3/Cd_{1-x}Zn_xS$ substrates were proceeded as follows. A mixed solution of $CdSO_4$, $Na_2S_2O_3$ and $Na_2Se_2O_3$ (or SeO_2) was used as the source of film deposition. The cathode potential and current density during the deposition were varied from – 0.1 to – 0.8 V and from 12 to 28 mA/cm^2, respectively. The film thickness was about 2 ÷ 9 μm. Concentration of charge carriers at 300 K was $2\times10^{16} \div 10^{17}$ cm^{-3} in $CdS_{1-y}Se_y$ films with $0.3 \le y \le 0.9$.

As ohmic contacts we used In for the $CdS_{1-y}Se_y$ and Ag for the In_2O_3. The ohmicity of the contacts was controlled by current-voltage characteristics (*I-V*). The active area of In_2O_3 / $Cd_{1-x}Zn_xS$ / $CdS_{1-y}Se_y$ heterostructures was 0.5 ÷ 3 cm^2.

3. Results and discussion

The dark current-voltage characteristics of the heterostructures were clearly asymmetric at 300 K (Fig. 1). The pass direction corresponds to positive polarity of the external bias on the $CdS_{1-y}Se_y$ films. At voltages $V = 1$ V the rectification in the as prepared structures $In_2O_3 / Cd_{0.5}Zn_{0.5}S / CdS_{0.2}Se_{0.8}$ reaches a value of 800 ÷ 900 (Fig. 1, curve 1) and smoothly decreases, when Zn concentration x increases and Se concentration y decreases (Fig. 1, curves 2 – 4). The forward current of the structures is described by the exponential dependence up to the cut-off voltage (V_d). Observed direct bias of *I-V* characteristics at different temperatures shows that forward currents mainly correspond to the recombination tunnel mechanism [12, 13]. With increasing forward bias $V \geq (0.7 \div 0.92)$ V a linear approximation of the *I-V* characteristics gives values $V_d = (0.48 \div 0.79)$ V for the structures with various x and y. Dependence of the type $I \sim V^n$ (were $n \geq 2$) is observed at relatively high voltages $V \geq (1 \div 1.4)$ V. It may be explained by the injection of charge carriers to $CdS_{1-y}Se_y$ films [11]. The reverse current of the structures obeys a linear law ($I \sim V$) at relatively low voltages $V \leq (1 \div 6)$ V and at the high voltages $V \geq (3 \div 7)$ V comes soft breakdown.

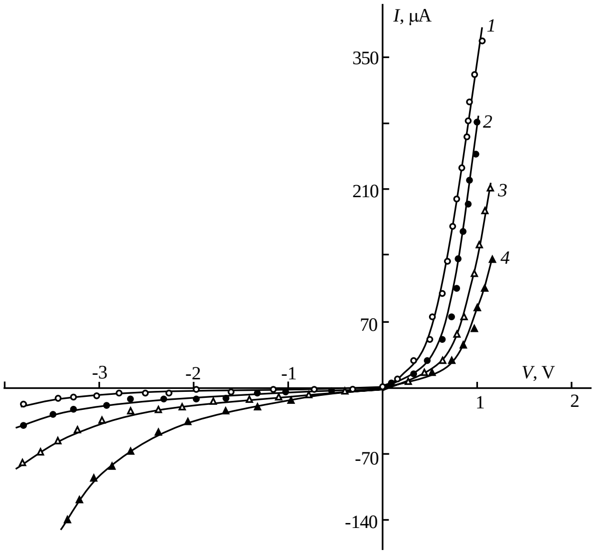

Fig. 1. The dark current-voltage characteristics of the as prepared $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ *heterostructures at* $T = 300$ *K for different* x *and* y *:* x *: 1 – 0.5; 2 – 0.6; 3 – 0.6; 4 – 0.7;* y *: 1 – 0.8; 2 – 0.8; 3 – 0.9; 4 – 0.9.*

The voltage dependence of capacitance in all investigated heterostructures are linear. The C^{-2}-V characteristics of the heterojunctions versus the *x* and *y*, are given in Fig. 2. Typical values of the diffusion potential V_d, obtained at intersection with voltage axis, was 0.54 V in $In_2O_3 / Cd_{0.5}Zn_{0.5}S / CdS_{0.2}Se_{0.8}$ heterostructures (Fig. 2, curve 1) and about 0.61 V in $In_2O_3 / Cd_{0.4}Zn_{0.6}S / CdS_{0.2}Se_{0.8}$ heterostructures (Fig. 2, curve 2). Observable change of V_d with increasing of x and y, is connected to change of band gap of the $Cd_{1-x}Zn_xS$ and $CdS_{1-y}Se_y$ films [14, 15].

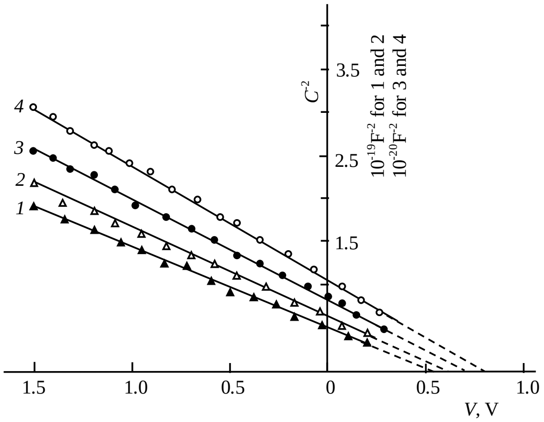

Fig. 2. $C^{-2} - V$ *characteristics of the as prepared* $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ *heterostructures at* $T = 300$ *K for different* x *and* y *:* x *: 1 – 0.5; 2 – 0.6; 3 – 0.6; 4 – 0.8;* y *: 1 – 0.8; 2 – 0.8; 3 – 0.9; 4 – 0.9.*

The values of V_d, experimentally found from *I-V* and *C-V* measurements, appreciably differ and as follows from the given figures, when Zn and Se concentration increases this divergence decreases (Fig. 1 and 2). It is supposed, that the increase x and y in films $Cd_{1-x}Zn_xS$ and $CdS_{1-y}Se_y$, leads, first, to increase of a potential barrier [14, 15], and, secondly, to decrease of concentration of the electric dipoles in the junction region, despite the fact that films In_2O_3 and $Cd_{0.4}Zn_{0.6}S$ have a poor lattice match with the films $CdS_{0.2}Se_{0.8}$ [16, 17].

Illumination of the heterostructures revealed a photovoltaic effect. The sign of the photovoltage does not depend on geometry of their illumination and is kept in all area of the photosensitivity. The open-circuit-photovoltage and short-circuit-photocurrent of the as prepared structures with various compositions at temperature 300 K and illumination 1500 Lx reached $V_{oc} = (0.22 \div 0.43)$ V and $J_{sc} = (0.58 \div 0.96)$ mA/cm^2, respectively.

The typical short-circuit-photocurrent (J_{sc}) spectrum of the as prepared heterostructures $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ has a single peak under illumination from the side of the $CdS_{1-y}Se_y$ films, which the peak corresponds to the band gap of $CdS_{1-y}Se_y$ films ($h\nu_1 = 1.94 \div 2.43$ eV). The sharp increase of a photocurrent is characteristic for them. Illumination of heterostructures $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ from the side of In_2O_3, leads to the shift of the long-wave edge to the short wavelength region of the spectrum. Thus the photosensitivity spectrum broadens, when *Zn* and *Se* concentration increases (Fig. 3, curves 1 - 4). It is necessary to note, that the width of photosensitivity spectrum was maximum in heterostructures, with more thin $Cd_{1-x}Zn_xS$ films (5 μm) (Fig. 3, curve 4).

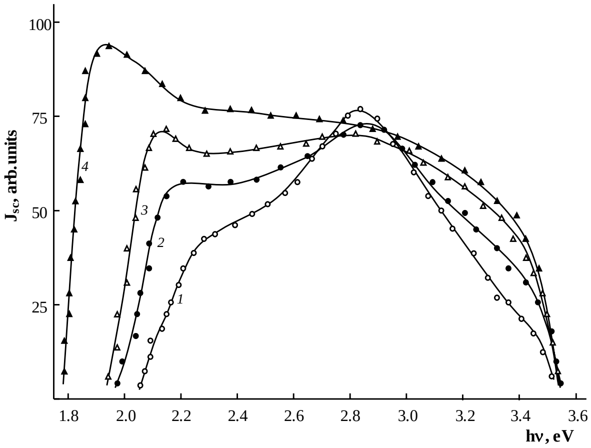

Fig. 3. Short-circuit-current spectrum illuminated from the side of In_2O_3, *as-deposited heterostructures* $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ *at* $T = 300$ *K for different* x *and* y: x: *1 – 0.4; 2 – 0.5; 3 – 0.5; 4 – 0.6;* y: *1 – 0.3; 2 – 0.5; 3 – 0.6; 4 – 0.8.*

We also studied the effect of heat-treatment on the photoelectric properties of these heterostructures. There occurs a reconstruction of the photosensitivity spectrum after heat-treatment, i.e. the spectrum broadens. The increase of heat-treatment temperature from 100 to 200 °C (at τ_a = 5 min) leads to sharply increase of photosensitivity of the $CdS_{0.2}Se_{0.8}$ films, and the photosensitivity of films $Cd_{0.4}Zn_{0.6}S$ thus remains almost constant (Fig. 4, curve 2). The further increase of heat-treatment temperature up to 380 ÷ 400 °C leads to sharp increase of the photosensitivity in the wavelength region of 0.354 ÷ 0.7 μm (Fig. 4, curve 3). The long-term annealing ($\tau_a \geq 15$ min) of heterostructures at temperatures $T_a \geq 400$ °C destroys them and leads to worsening of their parameters (Fig. 4, curves 4, 5).

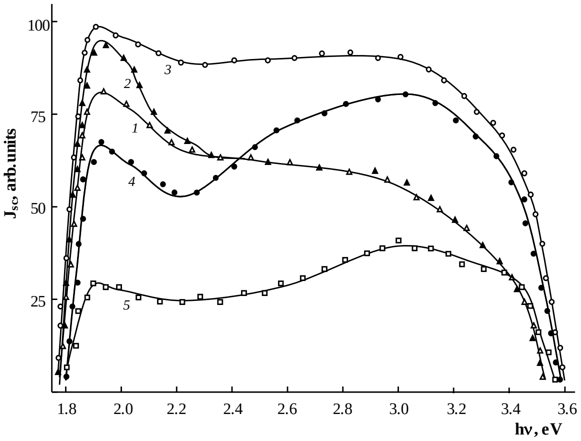

Fig. 4. Short-circuit-current spectrum of the heterostructures $In_2O_3 / Cd_{0.4}Zn_{0.6}S / CdS_{0.2}Se_{0.8}$ *versus annealing temperature* (T_a) *and time* (τ_a): T_a, *°C: 1 – 0; 2 – 200; 3 – 400; 4 – 420; 5 – 480 ;* τ_a, *min: 1 – 0; 2 – 5; 3 – 7; 4 – 9; 5 – 18.*

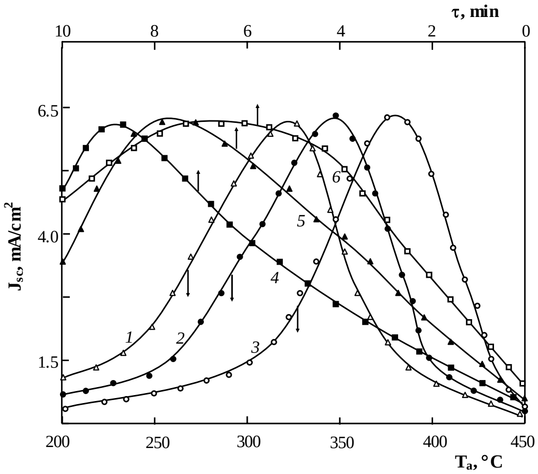

Fig. 5. Dependence of short-circuit-photocurrent on the annealing temperature (1 – 3) and time (4 – 6) in $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ *heterostructures for different* x *and* y: x: *1, 4 – 0.4; 2, 5 – 0.5; 3, 6 – 0.6;* y: *1, 4 – 1; 2, 5 – 0.9; 3, 6 – 0.8.*

The value of short-circuit-photocurrent varies nonmonotonically with annealing temperature and duration (Fig. 5). Initially, J_{sc} increases with T_a and τ_a, reaches a maximum value and at $\tau_a \geq 9$ min, decreases drastically (Fig. 5, curves 2 - 5). The maximum in the J_{sc} (T_a) curves shifts to longer T_a (Fig. 5, curves 1 – 3) and $J_{sc}(\tau_a)$ curves shifts to shorter τ_a (Fig. 5, curves 4 - 6) with increasing x and decreasing y. The maximal values of open-circuit-photovoltage and short-circuit-photocurrent at temperature 300 K and illumination 1500 Lx, of the heterostructures $In_2O_3 / Cd_{0.4}Zn_{0.6}S / CdS_{0.2}Se_{0.8}$ annealed in air at temperatures T_a = 380 ÷ 400°C for τ_a = 7 min reached 0.48 V and 5.9 ÷ 6.3 mA/cm^2, respectively.

The observable changes in parameters of heterostructures after heat-treatment are explained in terms of an electron-molecular interaction of the structures with the oxygen [18,19].

It should be emphasized that the parameters were quite reproducible and did not show signs of any degradation processes over the time of the investigation (8 ÷ 9 month).

4. Conclusion

By varying the composition of the films $Cd_{1-x}Zn_xS$, $CdS_{1-y}Se_y$ and heat-treatment regime it is possible to fabricate special photosensitive heterostructures $In_2O_3 / Cd_{1-x}Zn_xS / CdS_{1-y}Se_y$ with controlled parameters, which can be used in optoelectronics and solar engineering.

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