Modeling of a solar cell based on Co_3O_4 and $(Co_3O_4)_{1-x}(ZnO)_x$ films

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Numerical simulation of a solar cell based on the heterojunction of nanocrystalline films of zinc oxide modified with cobalt oxide $(Co_3O_4)_{1-x}(ZnO)_x$ and cobalt oxide (Co_3O_4) formed by solid-phase pyrolysis is carried out. The effect of the electron affinity of $(Co_3O_4)_{1-x}(ZnO)_x$ films, the thickness of the Co_3O_4 layer and the concentration of acceptors in it on the photoelectric parameters has been studied.

Keywords: solar cell, heterojunction, photovoltaic parameters.

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1. Introduction

Some of the most suitable materials for solar cells based on the $p-n$ junction are semiconductor metal oxides, among which zinc oxide (ZnO) and cobalt oxide (Co_3O_4) [1] are widely used, as well as composite nanomaterials based on them [2]. Previously, using low-temperature solid-phase pyrolysis, we formed films of pure zinc oxide, zinc oxide modified with cobalt oxide $(Co_3O_4)_{1-x}(ZnO)_x$ [3] and tin oxide (SnO_2-ZnO) [4,5]. These films exhibit photovoltaic [3,6] and gas-sensitive [4] properties. The introduction of a second oxide into the ZnO structure changes the electron work function, electron affinity, and band gap [5,6].

2. Experiment

Thin nanocomposite Co_3O_4 films and $(Co_3O_4)_{1-x}(ZnO)_x$ films with a Co:Zn ratio from 1:99 to 10:90 were synthesized by solid-phase pyrolysis on polycor substrates, and their structural, optical and electrical parameters were measured [3,6]. Modification of zinc oxide with cobalt oxide allows to vary their optical, electrophysical and surface properties. The band gap, resistivity, concentration and mobility of charge carriers were measured for the resulting films. These data were used in computing simulation (see the Table).

In this work, the simulation of solar cells based on the heterojunction of Co_3O_4 and $(Co_3O_4)_{1-x}(ZnO)_x$ films was carried out in the computing simulation program SCAPS-1D. A special feature of this program is that it takes into account the opportunity of charge carrier tunneling at heterojunctions [7–10]. Tunneling processes can occur in films $(Co_3O_4)_{1-x}(ZnO)_x$, since $p-n$ junctions in their structure contribute to the existence of internal electric fields [6,8].

The solar cell consisted of a front contact based on indium tin oxide (ITO), a photoactive layer n-type $(Co_3O_4)_{1-x}(ZnO)_x$, a photoactive layer p-type Co_3O_4, and a rear contact (Ni). For semiconductor layers, the effective cross section for electron and hole capture by a defect was taken to be equal to $2 \cdot 10^{-14}$ cm^2, and the thermal velocity of charge carriers — 10^7 cm/s. The band gap for Co_3O_4 was 1.6 eV, and for $(Co_3O_4)_{1-x}(ZnO)_x$ – 3.13 eV. The electron affinity (χ) for the layer $(Co_3O_4)_{1-x}(ZnO)_x$ varied within 4.48–4.9 eV.

In the simulation, it was assumed that the main defects in the Co_3O_4 layer are oxygen vacancies, which are also acceptors. The recombination mechanism was described according to the Shockley–Reed–Hall theory. The work function from the front contact (ITO) was 4.4 eV, and from the rear contact (Ni) — 5 eV [11].

3. Results and discussion

Variable parameters affecting the photovoltaic parameters of solar cells are the electron affinity of films $(Co_3O_4)_{1-x}(ZnO)_x$, layer thickness and acceptor concentration in the layer Co_3O_4. Figure 1 presents the dependence of efficiency, no-load voltage (U_{oc}) and short-circuit current density (J_{sc}) on these parameters when changing electron affinity (χ).

From the figure it can be concluded that the film $(Co_3O_4)_{1-x}(ZnO)_x$, in which the parameter χ is equal to 4.48 eV, has the highest efficiency, no-load voltage and short-

Physical parameters of solar cell structure materials ITO/n-$(Co_3O_4)_{1-x}(ZnO)_x$/p-Co_3O_4/Ni

Parameters	p-Co_3O_4	n-$(Co_3O_4)_{1-x}(ZnO)_x$
Thickness, nm	200	100
N_A, cm^{-3}	$10^{12}-10^{17}$	–
N_D, cm^{-3}	–	10^{14}
E_g, eV	1.6	3.13
χ, eV	4	4.48–4.9
N_C/N_V, cm^{-3}	$2 \cdot 10^{17}/1.1 \cdot 10^{19}$	$2.2 \cdot 10^{18}/1.8 \cdot 10^{19}$
μ_n/μ_p, cm^2/(B · s)	100/1.5	100/25

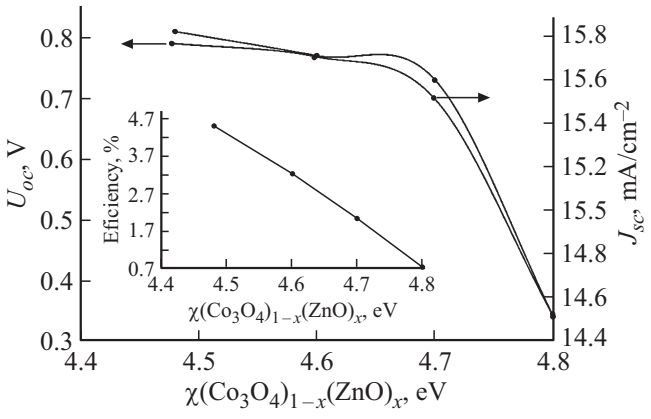

Figure 1. Dependence of no-load voltage, short circuit current density and efficiency (see inset) on the electron affinity of the film $(Co_3O_4)_{1-x}(ZnO)_x$.

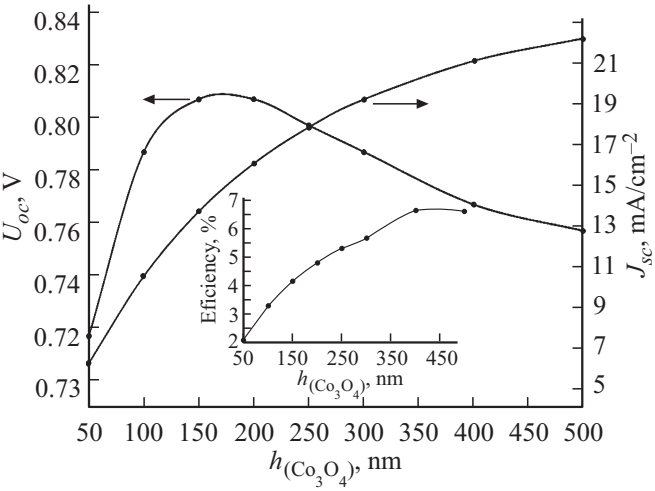

Figure 2. Effect of layer thickness Co_3O_4 on no-load voltage, short-circuit current density and efficiency (see inset).

circuit current density. The values U_{oc} and J_{sc} decrease slightly with increasing parameter χ up to 4.7 eV, then the drop becomes sharper. In this case, the efficiency decreases linearly. This is explained by the fact that as χ increases, the potential barrier that appears at the heterojunction boundary becomes higher, which prevents the transfer of charge carriers through it.

For further simulation of the dependence of the photovoltaic parameters of the solar cell on the concentration of acceptors in the Co_3O_4 layer, the value χ was taken equal to 4.48 eV. Calculations have shown that an increase in the concentration of acceptors in the Co_3O_4 layer from 10^{12} to 10^{17} cm^{-3} leads to a decrease in the short-circuit current density from 15.78 to 11.05 mA/cm^2 and to an increase in the no-load voltage from 0.72 to 2.74 V. The latter is associated with an increase in the saturation current density (J_0) [10–12].

The value of V_{oc} is limited by the value of J_0, which decreases as Na increases. The optimal concentration of acceptors of the photoactive layer Co_3O_4 is $\sim 10^{14}$ cm^{-3}. The results of simulation of the influence of the thickness (h) of the Co_3O_4 layer on the photovoltaic parameters are shown in Figure 2. The following parameters were used: $\chi(Co_3O_4)_{1-x}(ZnO)_x = 4.48$ eV, the thickness of the layer $(Co_3O_4)_{1-x}(ZnO)_x$ is 100 nm, the concentration of acceptors in the layer Co_3O_4.

The figure shows that the best photovoltaic characteristics (efficiency — 6.62%, $J_0 = 20.79$ mA/cm^2, $V_{oc} = 0.77$ V, filling factor — 38.7%) are achieved with a thickness of h with Co_3O_4 layer equal to 400 nm. The presence of a maximum is due to the fact that with increasing film thickness, the short-circuit current increases, which tends to saturation, while the no-load voltage decreases due to an increase in the recombination rate [11,12]. The obtained simulation results are better than the parameters of a solar cell based on the Co_3O_4/ZnO heterojunction, which was studied in the work [13]. Here V_{oc} was 14 mV, J_{sc} — $\sim 20\,\mu$A/cm^2, the filling factor (FF) was 0.25, and the energy conversion efficiency was only $7 \cdot 10^{-5}$%. The small value of the efficiency index obtained in the work [13], as shown in Figure 1, can be associated with the high electron affinity of the ZnO film. In addition, in the work [13] the thickness of the Co_3O_4 layer is 250 nm, and this, as can be seen from Figure 2, is not optimal.

4. Conclusion

The simulation showed that the formation of solar cells based on the heterojunction of Co_3O_4 and $(Co_3O_4)_{1-x}(ZnO)_x$ films formed by solid-phase pyrolysis is promising, since by varying the concentration of Co_3O_4 in the film $(Co_3O_4)_{1-x}(ZnO)_x$, its electrophysical characteristics that allow to obtain higher photovoltaic parameters can be selected. The optimal parameters of the structure of the solar cell were obtained at the thickness of the layer Co_3O_4 (400 nm), the concentration of acceptors (10^{14} cm^{-3}) in it, the value of electron affinity in the layer $(Co_3O_4)_{1-x}(ZnO)_x$ (4.48 eV). The solar cell demonstrated the following photovoltaic parameters: efficiency — 6.62%, short-circuit current density — 20.79 mA/cm^2, no-load voltage — 0.77 V, fill factor — 38.7%.

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Conflict of interest

The authors declare that they have no conflict of interest.

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