Conference materials
UDC 621.383
DOI: https://doi.org/10.18721/JPM.163.139

Research of the photoelectric parameters of ZnO/Cu_2O heterojunction solar cells

A.V. Saenko ✉, G.E. Bilyk, S.P. Malyukov

Southern Federal University, Taganrog, Russia

✉ avsaenko@sfedu.ru

Abstract. Theoretical modeling of ZnO/Cu_2O heterojunction solar cells has been carried out to optimize its structure and increase the energy conversion efficiency. The effect of the thickness and defect concentration in Cu_2O and ZnO layers on the efficiency of a solar cell is studied. It was found that the optimal thickness of the Cu_2O and ZnO layers should be 5 μm and 20 nm, respectively. It is shown that to obtain a high efficiency of a solar cell, the defect concentration (copper vacancies) in the Cu_2O layer should be 10^{15} cm^{-3}, and the defect concentration (oxygen vacancies) in the ZnO layer should be 10^{19} cm^{-3}. The maximum efficiency of a solar cell based on ZnO/Cu_2O is 6 %. The experimental formation of Cu_2O and ZnO layers by magnetron sputtering at room temperature has been carried out, their surface morphology has been studied, and experimental samples of oxide solar cells have been created.

Keywords: numerical simulation, oxide semiconductors, layer thickness, defect concentration, solar cell, photovoltaic parameters, magnetron sputtering

Funding: The study was supported by the grant of Russian Science Foundation No. 23-29-00827, https://rscf.ru/project/23-29-00827/ at the Southern Federal University.

Citation: Saenko A.V., Bilyk G.E., Malyukov S.P., Research of the photoelectric parameters of ZnO/Cu_2O heterojunction solar cells, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 221–226. DOI: https://doi.org/10.18721/JPM.163.139

Материалы конференции
УДК 621.383
DOI: https://doi.org/10.18721/JPM.163.139

Исследование фотоэлектрических параметров солнечных элементов с гетеропереходом ZnO/Cu_2O

А.В. Саенко ✉, Г.Е. Билык, С.П. Малюков

Южный федеральный университет, г. Таганрог, Россия

✉ avsaenko@sfedu.ru

Аннотация. Проведено теоретическое моделирование солнечного элемента с гетеропереходом ZnO/Cu_2O для оптимизации его структуры и повышения эффективности преобразования энергии. Исследовано влияние толщины и концентрации дефектов в слоях Cu_2O и ZnO на эффективность солнечного элемента. Получено, что оптимальная толщина слоев Cu_2O и ZnO должна составлять 5 мкм и 20 нм соответственно. Показано, что для получения высокой эффективности солнечного элемента концентрация дефектов (вакансий меди) в слое Cu_2O должна быть 10^{15} см$^{-3}$, а концентрация дефектов (кислородных вакансий) в слое ZnO должна быть 10^{19} см$^{-3}$. Получена максимальная эффективность солнечного элемента на основе ZnO/Cu_2O равная 6 %. Проведено экспериментальное формирование методом магнетронного распыления при комнатной температуре слоев Cu_2O и ZnO, исследована их морфология поверхности и созданы экспериментальные образцы оксидных солнечных элементов.

Ключевые слова: численное моделирование, оксидные полупроводники, толщина слоев, концентрация дефектов, фотоэлектрические параметры, солнечный элемент, магнетронное распыление

Финансирование: Исследование выполнено за счет гранта Российского научного фонда № 23-29-00827, https://rscf.ru/project/23-29-00827/ в Южном федеральном университете.

Ссылка при цитировании: Саенко А.В., Билык Г.Е., Малюков С.П. Исследование фотоэлектрических параметров солнечных элементов с гетеропереходом ZnO/Cu_2O // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 221–226. DOI: https://doi.org/10.18721/JPM.163.139

Introduction

Recently, there has been a significant increase in interest in the development of solar cells based on a heterojunction of two oxide semiconductors, since they have the potential to reduce manufacturing costs, as well as being chemically stable and environmentally friendly materials. The prospects for the use of oxide semiconductors ZnO and Cu_2O are mainly associated with a suitable energy band structure and high thermal stability. For practical applications, it is interesting to form oxide solar cells on a flexible substrate (polyethylene terephthalate, PET). Solar cells based on Cu_2O have a theoretical limit of energy conversion efficiency according to Shockley-Quisser of the order of 15–20 %. However, the maximum efficiency of oxide solar cells is still only 1–2 %, which is associated with the quality of the deposited oxide layers and metal contacts, the absorption coefficient of the layers, and the quality of the interfaces [1, 2]. Currently, various methods for obtaining heterojunctions based on ZnO/Cu_2O are being actively developed to achieve high efficiency of solar cells. The difficulty in creating a heterojunction lies in the presence of a high defect concentration, which leads to significant recombination losses and leakage currents. Thus, it is necessary to carry out theoretical and experimental studies of solar cells based on the ZnO/Cu_2O heterojunction in order to optimize their structure and achieve maximum efficiency.

In this work, a model of a solar cell based on a ZnO/Cu_2O heterojunction was created in the SCAPS numerical simulation program and a study was made of the effect of the thickness and defect concentration in Cu_2O and ZnO layers on the photovoltaic parameters of a solar cell. The formation of Cu_2O and ZnO layers by magnetron sputtering at room temperature (25 °C) in an oxygen-free environment was also carried out, their surface morphology was studied, and experimental samples of oxide solar cells were created.

Materials and Methods

To plot the current-voltage characteristics and obtain photovoltaic parameters of solar cells, such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and efficiency (η), the SCAPS one-dimensional numerical simulation program was used, which is based on a non-stationary diffusion-drift system of semiconductor equations [3, 4]:

$$\frac{\partial}{\partial x}\left[\mu_n\left(-n\frac{\partial\varphi}{\partial x}+\frac{kT}{q}\frac{\partial n}{\partial x}\right)\right]+G-R=\frac{\partial n}{\partial t}, \quad (1)$$

$$\frac{\partial}{\partial x}\left[\mu_p\left(p\frac{\partial\varphi}{\partial x}+\frac{kT}{q}\frac{\partial p}{\partial x}\right)\right]+G-R=\frac{\partial p}{\partial t}, \quad (2)$$

$$\frac{\partial^2\varphi}{\partial x^2}=-\frac{q}{\varepsilon\varepsilon_0}\left(p-n-N_A+N_D+p_t-n_t\right), \quad (3)$$

where n, p are the concentration of free electrons and holes, μ_n, μ_p are the electron and hole mobilities, φ is the electric potential, k is the Boltzmann constant, T is temperature; q is the elementary charge, ε is the relative permittivity, ε_0 is the dielectric constant, G is the rate of optical generation of electron-hole pairs, R is the rate of recombination of electron-hole pairs, N_D, N_A are the concentrations of the donor and acceptor dopants, n_t, p_t are the density of traps (defects) for electrons and holes.

The structure of a solar cell was considered, consisting of an oxide heterojunction and two contacts: a front contact (AZO/ITO), an n-type transparent window layer (ZnO), a p-type photoactive layer (Cu_2O), and a rear contact (Au/Cu). The main physical parameters of materials used in modeling the structure of a solar cell are taken from [4–6]. To calculate the absorption coefficients (α) of the Cu_2O and ZnO layers as a function of the wavelength (λ) of the incident radiation, the traditional SCAPS model for optical absorption was used:

$$\alpha(\lambda) = A\sqrt{\frac{hc}{\lambda} - E_g}, \tag{4}$$

where h is the Planck constant, c is the speed of light in vacuum, E_g is the band gap of Cu_2O (2.1 eV) and ZnO (3.4 eV), A is the absorption constant (10^5 $cm^{-1}\cdot eV^{-1/2}$). The calculations were carried out in the wavelength ranges 200–360 nm for ZnO and 200–590 nm for Cu_2O.

In modeling, it was assumed that the main defects in the ZnO layer are oxygen vacancies, which are also donors, and the main defects in the Cu_2O layer are copper vacancies, which are acceptors [7]. The defect concentration at the Cu_2O/ZnO interface was set equal to 10^{12} cm^{-2}, and the effective cross section for the capture of electrons and holes by a defect was taken to be 10^{-13} cm^2. The work function of the front contact was 4.2 eV, and the work function of the rear contact was 5.1 eV. The value of the series resistance in the solar cell was 3.3 $\Omega\cdot cm^2$, and the value of the shunt resistance was 2500 $\Omega\cdot cm^2$ [6].

In addition to numerical simulation, the formation of ZnO and Cu_2O layers on glass and silicon substrates was carried out by radio-frequency (RF) magnetron sputtering on a VSE-PVD-DESK-PRO setup ("AcademVak") from ceramic targets at room temperature in an oxygen-free environment. The magnetron sputtering method does not require a high temperature for film deposition and makes it possible to use various materials as substrates. ZnO and Cu_2O layers were obtained at a plasma discharge power of 75 W and an operating pressure of $5\cdot10^{-3}$ mbar. The film surface morphology was studied using a Nova Nanolab 600 (FEI Company) scanning electron microscope. The surface roughness was studied by atomic force microscopy (AFM) in the semi-contact mode at the NTEGRA nanolaboratory (NT-MDT). The current-voltage characteristics of the obtained heterostructures were measured using a R33 resistance box in a two-electrode circuit with pressure point contacts based on a National Instruments PXI-1004 complex under illumination with a halogen lamp with a radiation intensity of 100 mW/cm^2.

Results and Discussion

The main factors affecting the photoelectric parameters of a solar cell are the thickness and defect concentration in the Cu_2O photoactive layer, since it absorbs solar radiation and generates electron-hole pairs (Fig. 1). To study the influence of the Cu_2O layer thickness on the photoelectric parameters of a solar cell, simulations were carried out for its thickness in the range from 100 nm to 6 μm and a defect concentration of 10^{16} cm^{-3}, as well as a ZnO layer thickness of 50 nm and a defect concentration of 10^{19} cm^{-3}.

Fig. 1, *a* shows that the efficiency of the solar cell increases sharply (from 1.07 % to 5.29 %) as the thickness of the Cu_2O layer increases to 3 μm, and then the increase becomes less pronounced (efficiency 5.69 % at thickness of the Cu_2O layer is 6 μm). This is due to the fact that with an increase in the thickness of the Cu_2O layer, a larger number of photons with a wavelength up to the absorption limit near 600 nm is absorbed, which leads to the generation of a larger number of excess charge carriers and, accordingly, an increase in the short circuit current density [6]. The value of 5 μm (efficiency 5.61 %) was chosen as the optimal thickness of the photoactive Cu_2O layer, since its further increase by each 1 μm leads to an increase in efficiency by less than 0.1 %. Also Fig. 1, *a* shows that an increase in a defect concentration (copper vacancies) in the Cu_2O layer from 10^{13} cm^{-3} to 10^{15} cm^{-3} leads to an increase in efficiency from 4.14 % to 5.98 %, and a further increase in a defect concentration to 10^{18} cm^{-3} leads to a decrease in efficiency to 0.88 %. This is due to the fact that as the defect concentration in the Cu_2O layer increases,

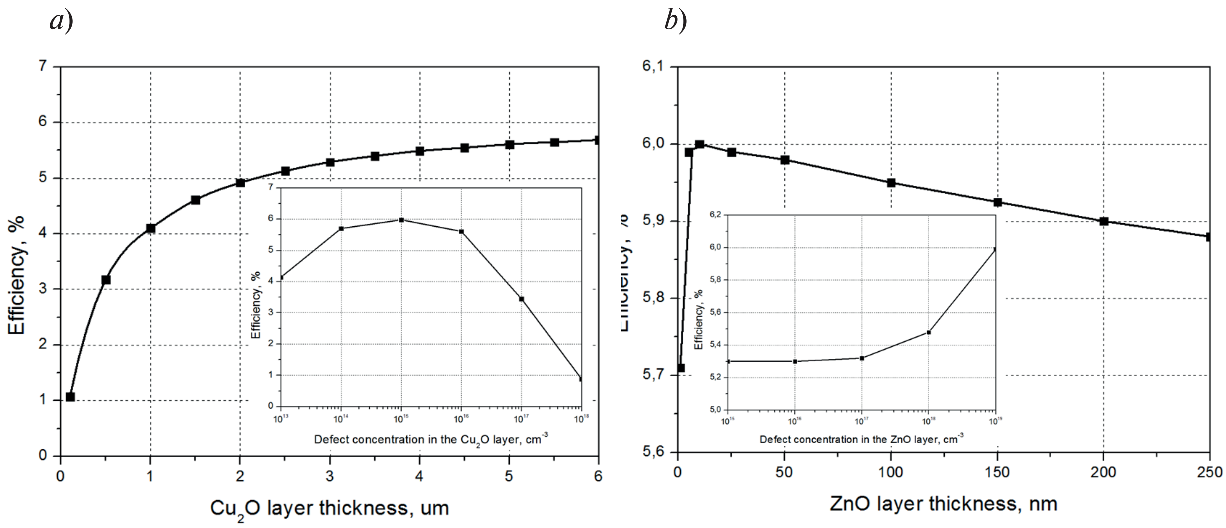

Fig. 1. Dependences of solar cell efficiency on the thickness and defect concentration in Cu_2O (*a*) and ZnO (*b*) layers

the concentration of acceptors (free charge carriers) also increases, but the diffusion length of charge carriers decreases, which first leads to an increase in the short circuit current density and then to a significant increase in the recombination rate and reduce the short circuit current density.

Important factors are the thickness and a defect concentration in the ZnO window layer, which contributes to the separation of the generated electron-hole pairs. To study the influence of the ZnO layer thickness on the photoelectric parameters of a solar cell, modeling was carried out for its thickness in the range from 1 nm to 250 nm and a defect concentration of 10^{19} cm^{-3}, as well as a Cu_2O layer thickness of 5 μm and a defect concentration of 10^{15} cm^{-3}.

Fig. 1, *b* shows that an increase in the thickness of the ZnO layer first leads to an increase in the efficiency of the solar cell to about 6% at a thickness of 5–35 nm due to the best separation of the generated electron-hole pairs, and then to a decrease to 5.88% (at 250 nm). A slight decrease in efficiency with increasing thickness is associated with a decrease in the short circuit current density due to an increase in the recombination rate caused by a small diffusion length of minority charge carriers (holes) equal to about 10 nm compared to the thickness of the ZnO layer. Also Fig. 1, *b* shows that an increase in the defect concentration in the ZnO layer from 10^{15} cm^{-3} to 10^{19} cm^{-3} leads to an increase in the efficiency of the solar cell from 5.3% to 6% and is associated with an increase in the open circuit voltage and small recombination losses in the ZnO layer due to its small thickness (20 nm).

Fig. 2 shows SEM and AFM images of ZnO and Cu_2O layers obtained by magnetron sputtering. Fig. 2, *a* shows that the surface morphology of the ZnO layer is uniform with an average grain size of 20–30 nm at a layer thickness of about 75 nm, and columnar formations characteristic of ZnO are observed on the transverse cleavage with a direction perpendicular to the layer plane [8]. Analysis of the AFM images showed that the ZnO layer has a relatively smooth surface with an average roughness value of 6.3 ± 2.1 nm. Fig. 2, *b* shows that the surface morphology of the Cu_2O layer is also uniform with an average grain size of 10–15 nm at a thickness of about 90 nm. An inconspicuous columnar structure appears on the Cu_2O transverse cleavage, which is often observed during low-temperature magnetron deposition of oxides, which is a consequence of the low mobility of deposited particles on the substrate surface [2]. Analysis of the AFM images showed that the Cu2O layer has a relatively smooth surface with an average roughness value of 3.2 ± 1.6 nm.

The first experimental samples of solar cells with the ITO (200 nm)/ZnO (50 nm)/Cu_2O (500 nm)/Cu (100 nm) structure were fabricated by magnetron sputtering and their current-voltage characteristics were measured. Fig. 3 shows the current-voltage characteristics obtained by approximating the experimental data for three samples with the same structure.

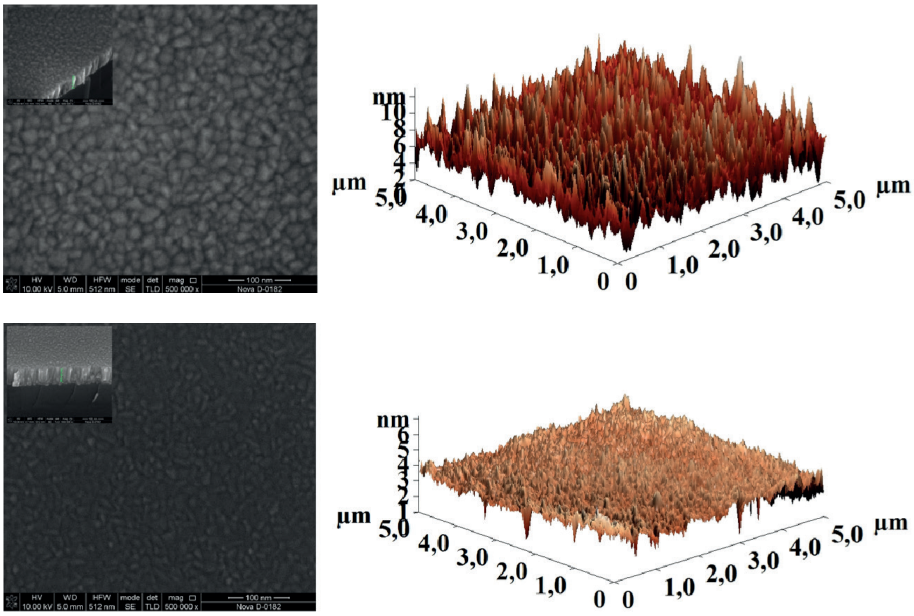

Fig 2. SEM and AFM images of ZnO (*a*) and Cu_2O (*b*) layers

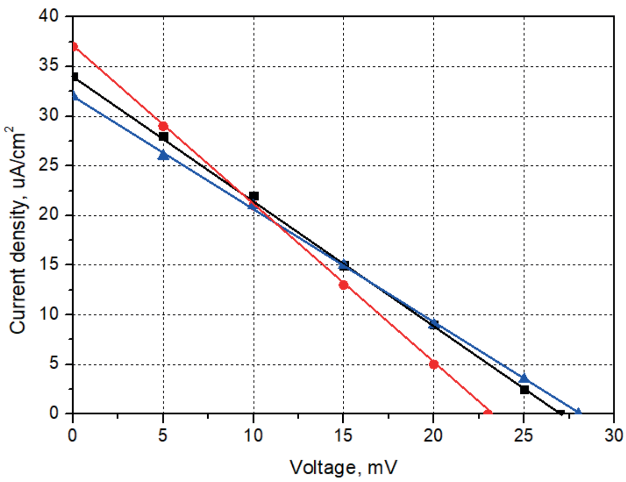

Fig. 3. Current-voltage characteristics of experimental samples of solar cells based on ZnO/Cu2O

Conclusion

This study shows the effect of the thickness and defect concentration in Cu_2O and ZnO layers on the efficiency of a solar cell. The optimal thicknesses of the Cu_2O and ZnO layers were determined, which were 5 µm and 20 nm, respectively. In addition, the optimal defect concentration in Cu_2O and ZnO layers (copper vacancies and oxygen vacancies) were determined, which amounted to 10^{15} cm^{-3} and 10^{19} cm^{-3}, respectively. Thus, the maximum efficiency of a solar cell based on ZnO/Cu_2O equal to 6 % was obtained (short circuit current density 11.25 mA/cm^2, open circuit voltage 0.68 V, fill factor 74.53%). The first experimental samples of oxide solar cells were obtained and their photovoltaic parameters were measured, which showed open-circuit voltage values in the range of 20–30 mV and short-circuit current density in the range of 30–40 $\mu A/cm^2$. The results can be used in the development and formation of oxide solar cell heterostructures.

REFERENCES

1. **Amador Perez-Tomas,** Functional Oxides for Photoneuromorphic Engineering: Toward a Solar Brain, Advanced Materials Interfaces. 6 (2019) 1900471.

2. **Bobkov A.A., Lashkova N.A., Maximov A.I., Moshnikov V.A., Nalimova S.S.,** Fabrication of oxide heterostructures for promising solar cells of a new generation, Semiconductors. 51 (2017) 61–65.

3. **Daniel A. Fentahun, Alekha Tyagi, Kamal K. Kar,** Numerically investigating the AZO/Cu_2O heterojunction solar cell using ZnO/CdS buffer layer, Optik – International Journal for Light and Electron Optics. 228 (2021) 166228.

4. **Saenko A.V., Klimin V.S., Rozhko A.A., Malyukov S.P.,** Modeling the Structure of an Oxide Solar Cell, Journal of Communications Technology and Electronics. 67 (2022) 108–114.

5. **Sung Hun Wee, Po-Shun Huang, Jung-Kun Lee, Amit Goyal,** Heteroepitaxial Cu_2O thin film solar cell on metallic substrates, Scientific RepoRts, 5 (2015) 16272.

6. **Saenko A.V., Malyukov S.P., Rozhko A.A.,** Modeling the structure of a lead-free perovskite solar cell, Applied Physics. 1 (2022) 19–27.

7. **Stefanovich G.B., Pergament A.L., Boriskov P.P., Kuroptev V.A., Stefanovich T.G.,** Charge transfer in rectifying oxide heterostructures and oxide access elements in ReRAM, Semiconductors. 50 (2016) 639–645.

8. **Agekyan V.F., Borisov E.V., Gudovskikh A.S., Kudryashov D.A., Monastyrenko A.O., Serov A.Yu., Filosofov N.G.,** Formation of Cu_2O and ZnO Crystal Layers by Magnetron Assisted Sputtering and Their Optical Characterization, Semiconductors. 52 (2018) 383–389.

THE AUTHORS

SAENKO Aleksandr V.
avsaenko@sfedu.ru
ORCID: 0000-0003-4206-4136

MALYUKOV Sergey P.
spmalyukov@sfedu.ru
ORCID: 0009-0004-0382-9719

BILYK German E.
bilyk@sfedu.ru
ORCID: 0009-0005-0891-7109

Received 06.07.2023. Approved after reviewing 18.07.2023. Accepted 18.07.2023.