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Structural and electrical characteristics of the ZnO/porous-Si/Si heterostructure: from synthesis to analysis of photocell efficiency

Abstract. The article deals with the step-by-step production of the ZnO/porous-Si/Si heterostructure: electrochemical etching of monocrystalline Si plates (100); deposition of ZnO films by the sol-gel method followed by centrifugation. A comprehensive study of the morphology of the obtained structure using a SEM and a AFM confirms the high degree of structural order of the obtained film and the presence of the main chemical elements of the ZnO:Al film on its surface. It was determined that the ZnO film has a thickness of 395 nm, while the porous-Si layer is 90 nm thick. An AFM showed that the surface of the material has a complex and heterogeneous structure with pronounced roughness. The maximum height of the profile is ~188 nm, indicating significant explosions and protrusions on the surface. The obtained values of the thickness and roughness of the manufactured structure were used to model the ZnO:Al/porous-Si/Si heterostructure in the PC1D program in order to find the optimal parameters of the solar cell. The values of no-load voltage, short-circuit current and maximum power were obtained from the simulation results, the filling factor and efficiency were calculated theoretically. Simulation results show that the fill factor of the fabricated structure is ~70.4%, and the efficiency of the ZnO/porous-Si/Si photoconverter is 22.4%. Increasing the level of doping to 10^{19} cm^{-3} leads to an increase in the efficiency of the photocell to a maximum value of 23%.

Key words: electrochemical etching, sol-gel method, heterostructure photoconverter, simulation.

Introduction

In the context of the world energy crisis and the desire for sustainable development, the search for new technologies for energy production becomes an important task. The modern problem of finding highly efficient and environmentally resistant materials for solar cells stimulates intensive scientific research in the field of photovoltaics. A promising approach to enhancing photoconverters is the utilization of ZnO/Si heterostructures, which are expected to increase the efficiency and stability of solar cells [1, 2]. The use of heterostructured solar cells based on ZnO/Si may have the potential for a number of advantages and prospects in photovoltaic devices: ZnO and Si are available and relatively cheap materials, which may affect the cost of solar cell production; ZnO

adheres well to silicon, which can facilitate the fabrication of heterostructures and provide stable contact between layers; ZnO/Si heterostructures can have low contact resistances, which facilitates injection current collection.

Recently, there have been reports on the prospects of using porous silicon as a buffer layer [3, 4]. This can allow to increase the surface contact area in the heterostructure, which, in turn, helps to increase the current in the solar cells. This innovative use of the buffer layer can improve the efficiency and performance of solar cells.

Thus, further research and development of ZnO/porous-Si/Si heterostructure solar cells remains relevant, as their potential can lead to the creation of more efficient and cost-effective photovoltaic devices for use in modern energy production technologies.

Literature review and problem statement

ZnO typically luminesces in the visible region of the spectrum, and this effect can be effectively exploited in photovoltaic applications. The shift of the spectra can be controlled by surface modification, doping and various post-synthesis materials treatments [5], which opens up additional possibilities for tuning the optical properties of heterostructures. Several methods were used to grow ZnO thin layers, such as thermal evaporation technique [6], chemical vapor deposition CVD [7], the method of HF magnetron sputtering [8], spray pyrolysis [9], pulsed laser deposition [10] and sol-gel method [11]. However, among these methods, sol-gel is one of the cheaper and easier to perform. In work [12], we obtained ZnO:Al films on porous Si (111) substrates by the sol-gel method followed by centrifugation.

An important tool for tuning the properties of the ZnO film according to the specific requirements and tasks of photovoltaic devices is the addition of doping impurities. In addition, alloying can also improve the resistance of the photocell to the influence of humidity, temperature and other factors, which can increase its service life. Usually, In, Al or Ga are used as alloying additives to obtain electrically conductive ZnO [13-15]. ZnO is known for its higher electron mobility and improved transparency in the wavelength range of $\lambda < 900$ nm [16], which plays a crucial role in enhancing the absorption intensity of light quanta. Doping with aluminum can cause a Burstein–Moss shift, which leads to an improvement in photosensitivity in the higher energy region, and a change in the concentration of charge carriers can affect the efficiency of charge collection and transport in the photocell. To improve the optical properties of the front layer, the authors of [17] proposed doping the ZnO film with ZnO:Ga gallium. Modeling of the resulting structures predicted a conversion efficiency of 19%, and a fill factor of 81%. Biruk Alebachew et al. [18] developed a Sn-doped ZnO layer, which was utilized in inverted organic solar cells (OSCs) based on the

commonly used poly-3-hexylthiophene (P3HT) polymer. The performance of the reference device improved from 1.01% to 3.45% after doping the ZnO layer with 3% Sn. This doping also increased the open-circuit voltage (V_{oc}) of the reference device (from 0.44 V to 0.61 V), attributed to a shift in the conduction band, which enhances charge transfer and reduces energy loss in the device.

Al doping of ZnO thin films allows creating a direct energy gap (E_g), increased from 3.50 to 3.80 eV with increasing Al doping [19]. The authors of this article found that the efficiency increased with increasing Al-doping and the highest efficiency at doping of 0.006 wt.% was 3.64% with $V_{oc}=2.8$ V, $J_{sc}=3.5$ mA/cm² and FF=0.371. Nunes et al. [20] tested ZnO:Al, obtaining $V_{oc}=0.49$ V, $J_{sc}=0.94$ mA/cm² and fill factor FF=0.39.

Investigate different design options and materials for photovoltaic structures to choose the most optimal option for specific needs, possibly with the help of simulations. Various programs are used to simulate photoconverters: Sentaurus TCAD [21], Solar Cell Capacitance Simulator (SCAPS) [22], Crosslight APSYS [23], a Personal Computer One Dimensional (PC1D) [24], Silvaco Atlas [25] and others. Among the listed, PC1D software is defined by its ease of use, flexibility of settings, wide range of research and availability for free use, which makes it a popular tool for solar cell simulation. The mathematical model used in the PC1D program is based on the Poisson equation, the Continuity Equation, as well as equations reflecting the processes of generation and recombination of charge carriers [26-28]:

$$\nabla \cdot (\varepsilon \nabla \phi) = -q(p - n + N_D - N_A),$$

$$\frac{\partial n}{\partial t} = \nabla \cdot (D_n \nabla n) + G_n - \frac{n - n_0}{\tau_{n_0}} + \frac{np - n_i^2}{\tau_{n_0}},$$

$$\frac{\partial p}{\partial t} = \nabla \cdot (D_p \nabla p) + G_p - \frac{p - p_0}{\tau_{p_0}} + \frac{np - n_i^2}{\tau_{p_0}},$$

$$J = q(D_n \nabla n - D_p \nabla p + \mu_n n \nabla \phi - \mu_p p \nabla \phi),$$

where ϕ is the potential that reflects the electric field; n and p – concentrations of electrons and holes; D_n and D_p are diffusion coefficients for electrons and holes; G_n and G_p – electron and hole generation rates; N_D and N_A – concentrations of donors and acceptors; n_i – concentration of intrinsic charge carriers; τ_{n_0} and τ_{p_0} is the recombination time of electrons and holes; q – elementary charge; ε is the dielectric constant.

The aim and objectives of the study

The purpose of this article is to obtain the ZnO/porous-Si/Si heterostructure and study the structural and photovoltaic parameters of solar cell photoconverters based on it in order to assess its potential for use in solar energy systems.

To achieve the set goal, it was necessary to complete a number of tasks:

- step-by-step production of the ZnO/porous-Si/Si heterostructure: electrochemical etching of monocrystalline Si(100) plates, deposition of a ZnO film by the sol-gel method followed by centrifugation;
- carrying out a comprehensive study of the morphology and structure of ZnO/porous-Si/Si;
- modeling parameters of photoconverters of ZnO/porous-Si/Si solar cells in the PC1D software package;
- study of the dependence of the efficiency on the level of doping of the ZnO film.

Materials and methods of research

Porous Si (100) was prepared according to the standard electrochemical etching method described in [29, 30]. After cleaning the traces of the herbivore and drying the substrates, a sol in the form of a gel was applied to their surface. The film-forming solution was a mixture of four different compounds [31]: zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, propan-2-ol C_3H_8O , N,N -dimethylpropan-1-amine $(CH_3)_2NCH_2$, 2-Methoxyethanol $C_3H_8O_2$. Aluminum chloride $AlCl_3 \cdot 6H_2O$ was used as an alloying reagent. The finished solution was

subjected to ultrasonic exposure (30 min). The resulting gel was deposited on porous Si substrates by the spin-coating method with a frequency of 3000 revolutions/minute for 30 seconds and heated 10 times in a furnace to a temperature of 350°C, and to 550°C in the final stage.

The morphology and cross-section of the obtained structure were examined using a JSM-6490 SEM. The chemical composition was determined by the EDAX method. The surface of the ZnO film was investigated using an AFM.

The PC1D program was used to calculate the parameters of ZnO/porous-Si/Si photoconverters. The parameters of the ZnO:Al/porous-Si/Si heterostructure (thickness of the layers, film roughness), parameters of the ZnO:Al film (width of the band gap; concentration, mobility, thermal velocity of charge carriers; recombination coefficients) were obtained from the scientific literature and are given in Table I, the parameters of the porous-Si and Si layers are given in [32]. The simulation was carried out at room temperature ($T=300$ K).

Table 1 – List of parameters used in the simulation [33-35]

Parameter	Value
<i>Layer ZnO:Al</i>	
Band gap, E_g	3.37 eV
Electron affinity, χ	4.5 eV
Dielectric constant, ε	8.49
N-type background doping	$1 \cdot 10^{18} \text{ cm}^{-3}$

Experimental Results and their Discussion

Study of the composition and properties of the structure

From fig. 1 shows that the ZnO film penetrates the porous Si substrate – there is no gap between Si and ZnO at the interface. The surface of the structure is covered with particles with a characteristic columnar structure, which is characteristic of zinc oxide. Elemental analysis of the surface of the structure was carried out by EDAX in the range of binding energy from 0 to 10 keV (Fig. 2). The spectrum peaks show the

presence of Zn, O, Si, Al. The appearance of Si is associated with the appearance of cracks in the film, which can be eliminated by adjusting the deposition process of the ZnO film. C and S

elements are also present in a small amount (~1%), which are reaction residues. The atomic percentage of the elements is presented in the tab of fig. 2.

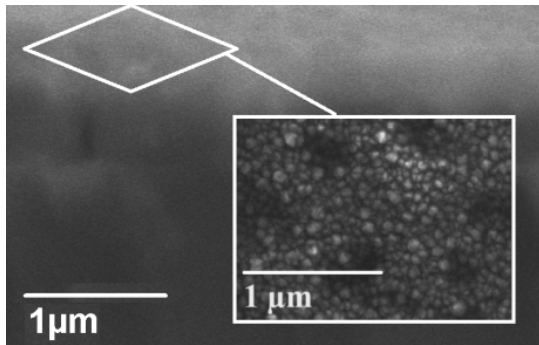


Figure 1 – The SEM-image of the surface and cross-section of the ZnO:Al/porous-Si/Si heterostructure

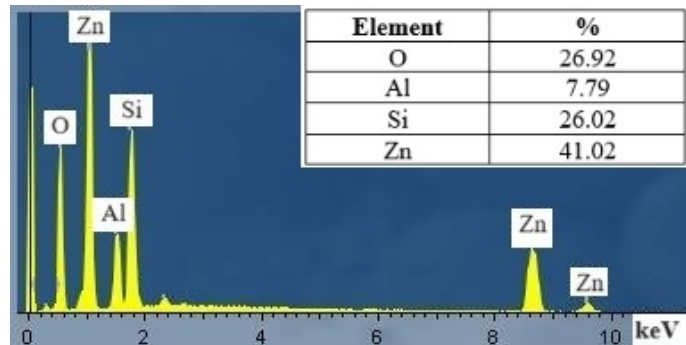


Figure 2 – EDAX analysis of ZnO films

In the future, the parameters of this structure will be used for modeling photoconverters of solar cells (Table 2).

surface indicates its complex and heterogeneous structure with pronounced roughness and height explosions, which can play an important role in the properties and applications of this material.

Table 2 – Layer thicknesses of the ZnO:Al/porous-Si/Si heterostructure

Parameter	Value
Layer thickness Si, mkm	500
Layer thickness porous-Si, nm	290
Layer thickness ZnO:Al, nm	395

The surface of the material, studied using an AFM, shows a high degree of roughness and heterogeneity (Fig. 3). The maximum height of the profile (Rmax) is 188 nm, indicating significant bumps and ridges on the surface. The highest point is at a distance of 379 nm above the baseline (Zmax), which may indicate the presence of pronounced irregularities or structures above the average level. The minimum value of the measured height (Zmin) reaches 566 nm, which indicates the presence of deep grooves or pits on the surface of the material. The overall "roughness" of the surface is ~22 nm, and the average surface height is Ra=17 nm, indicating height scatter and surface roughness. The general description of the

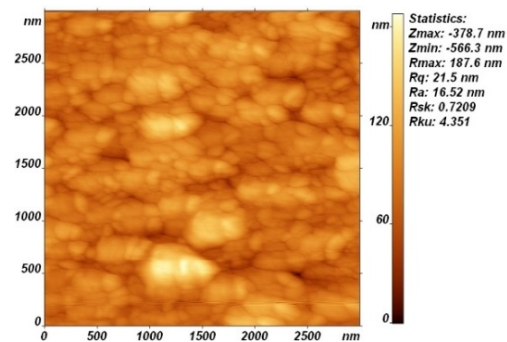


Figure 3 – The AFM image of the surface of ZnO:Al/porous-Si/Si(100) heterostructures.

Simulation results and it's discussion

The obtained values of the thickness and roughness of the manufactured structure were used to model the ZnO:Al/porous-Si/Si heterostructure in the PC1D program to find the optimized parameters of the solar cell. Based on the simulation results, the no-load voltage, short-circuit current, and maximum power were obtained. The filling factor and efficiency were calculated according to the formulas [36, 37]:

$$FF = \frac{I_{max} \cdot V_{max}}{V_{OC} \cdot I_{SC}},$$

$$\eta = V_{OC} \cdot I_{SC} \cdot FF.$$

In Fig. 4 shows the current-voltage characteristics of the ZnO:Al/porous-Si/Si photoconverter.

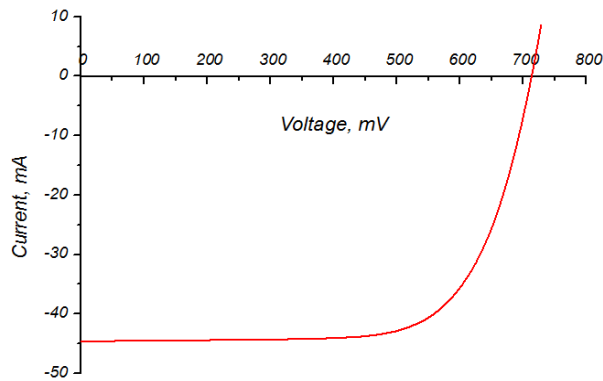


Figure 4 – The current-voltage characteristics of the photoconverter ZnO:Al/porous-Si/Si(100)

According to the obtained data and calculations, the fill factor of the fabricated structure is approximately 70.4%, and the efficiency is 22.4%.

Influence of doping on photovoltaic characteristics

Changing the doping level of the photoconverter window layer can affect its conductivity, transparency, contact with the photoconverter, electron output efficiency, recombination rate, and electrical capacity. Optimizing these parameters is essential for enhancing the efficiency and performance of the solar cell. To this end, a model of the ZnO/porous-Si/Si(100) heterostructure was developed, with doping levels (N_D) ranging from 10^{16} to 10^{21} cm^{-3} . Figure 5 presents graphs illustrating the relationship between the short-circuit current, open-circuit voltage, and efficiency of the ZnO/porous-Si/Si(100) photocell as a function of the doping level.

The analysis of the obtained data (Fig. 4) shows that increasing the level of doping of the

ZnO:Al layer from 10^{16} to 10^{19} cm^{-3} the I_{sc} current remains unchanged, and at doping values of 10^{20} cm^{-3} and below it begins to decrease. Most likely, this is due to the recombination of excess carrier charges, which reduces the I_{sc} current. The same is observed for the efficiency, which initially increases to 23.0% at a doping value of 10^{19} cm^{-3} , and then decreases.

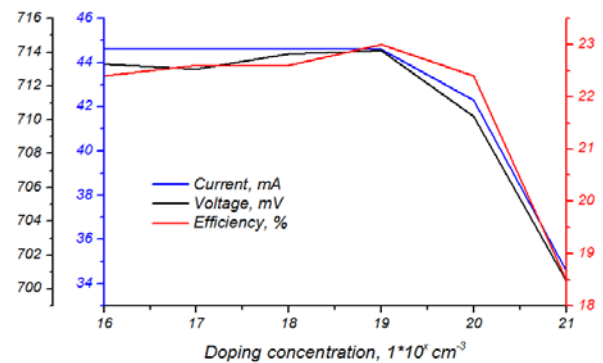


Figure 5 – The dependences of the open circuit voltage V_{oc} , short circuit current I_{sc} and efficiency η of the simulated solar cell on the doping level of the ZnO:Al layer.

The maximum V_{oc} no-load voltage value is reached at a doping value of 10^{19} cm^{-3} ($V_{oc}=714.1$ mV). However, at a high level of doping $>10^{19}$ cm^{-3} , there is a decrease in the efficiency of the interaction of photons with the semiconductor, which leads to a decrease in V_{oc} .

Considering the obtained results, the issue of optimization of ZnO:Al/porous-Si/Si photoconverters deserves further in-depth study. Future research may focus on optimizing the doping level of ZnO to find a balance between electrical conductivity and optical transparency by experimenting with different types of dopants (Ga, B, etc.) and their concentrations. In addition, in the future, attention should be paid to improving the homogeneity of doping, since the uneven distribution of impurities can affect the efficiency of photoconversion. Future research can focus on studying the effect of the size and uniformity of porous silicon and methods of passivating its surface to reduce recombination losses and increase the efficiency

of photovoltaic cells. The use of nanostructured ZnO coatings, which can be obtained by a controlled, relatively inexpensive method of thermal decomposition [38], will also improve light collection and reduce reflection and recombination losses.

Conclusion

Solar cells with heterostructures based on ZnO/porous-Si/Si can play a key role in providing an efficient and environmentally friendly energy source. The paper describes the process of obtaining porous Si (100) by means of electrochemical etching followed by applying a sol-gel solution to the surface of the substrates and heating them to 550°C. The morphology and chemical composition of the structure were investigated using scanning electron and atomic force microscopes. The general description of the surface indicates its complex structure with pronounced roughness,

which can affect the properties and application of this material. The PC1D program was used to model the photoconverters based on the manufactured structure. Based on the obtained data and calculations, the efficiency of the fabricated structure is 22.4%. It was determined that increasing the doping level of the ZnO layer to 10^{19} cm^{-3} results in the photocell achieving maximum efficiency (23.0%). However, at doping levels exceeding 10^{19} cm^{-3} , the efficiency of photon interaction with the semiconductor decreases.

This article is devoted to revealing the potential of ZnO/porous-Si/Si as a promising heterostructure for photoconverters of solar cells, and aims to contribute to the further development of photovoltaic technologies. The ZnO/porous-Si/Si heterostructure can be used in the manufacture of photodetectors, phototransistors or other devices for optical reading. This can be important in modern communication technologies and sensor systems.

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