Oxide Heterostructures for Photovoltaic Cells

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Abstract—A new technology of n-ZnO/p-CuO heterostructures formation within a single technological cycle by using the method of RF magnetron reactive sputtering of the powders of copper and zinc oxides has been proposed. The thin-film samples of oxide structures with the sequence of layers Glass/n-ZnO/i-ZnO/p-CuOx/Me were produced. Optical and structural properties of the CuO films and electrical properties of ZnO/CuO structures were investigated upon thermal treatment. It is shown that a photosensitive n-ZnO/p-CuO heterojunction may be formed by rapid (~1 min) thermal processing in air.

I. INTRODUCTION

The problem of creation of alternative sources of energy is relevant in today’s world. One of the known sources is solar energy, but the work on developing the most efficient structures and technologies is conducted to this day, revealing to the world all the new features, so now one of the most important tasks is finding the most effective in production and operation of solar cells. This article is devoted to obtaining a solar cell based on oxide heterostructures.

Oxide films are widely used in electronic and optoelectronic [1], [2] applications. In recent years, there are new ideas to the development of heterohpse oxide systems [3]-[5] and oxide heterostructures [6], [7] for photovoltaic cells. Of interest are the perovskite oxides [8], [9] and semiconductor oxides [10].

Among new promising photoactive materials some oxide semiconductors such as Cu2O, CuO, ZnO and heterostructures on their basis take a special place. The advantages of oxide systems are their environmental friendliness during manufacturing, operation and disposal. However, the present problem of use these materials for photovoltaic solar cells is characterized by low efficiency and irreproducibility experimental results.

CuO and p-type Cu2O oxide semiconductors have great potential in use as an active layer of the solar cell due to the fact that these materials are of low cost, are widely distributed in the world, have a bandgap in the range of 1.21...2.1 eV [10], relatively high coefficient of absorption spectrum of sunlight. For Cu2O the theoretical estimation of converting efficiency of solar energy into electrical energy is 9...12%.

ZnO as an n-type inorganic semiconductor, is widely used in photovoltaics as an electron collection and hole blocking material due to its salient characteristics such as good optoelectronic properties, easy synthesis, non-toxicity. It has optical band gap at room temperature in the range of 3.1...3.3 [11].

For ZnO / CuO heterojunctions variety of methods including solid state synthesis, pressing, co-precipitation, sol-gel method, magnetron sputtering, thermal oxidation and hydrothermal method were applied [12]-[15] and methods of treating zinc oxide [16]-[18].

In the [19] solar cell structures based on CuO/ZnO were prepared by electrodeposition. Obtained heterostructures characterized by a high optical absorption in the wavelength range from 400 to 800 nm. In the polycrystalline form it is found, that despite the various types of crystal lattices, there is good physical and chemical compatibility. For polycrystalline CuO films band gap width (1.2 eV) and crystallite size (49 nm) are identified. Authors suggest that an increase in crystallinity increases the efficiency of solar cells. It is assumed that the heterostructure CuO/ZnO relates to the second type (covariant structures) heterostructures, and energy levels of the bands of CuO is higher than ZnO energy levels.

However, the present problem of use of photovoltaic solar energy based on the oxide heterostructures is characterized by low efficiency and irreproducibility experimental results. In [14] the solar cell structure, composed of a silver electrode, absorbing p-CuO layer, transparent n-ZnO:Sn layer, was obtained by vacuum deposition. Obtained research structure showed the following characteristics: open circuit voltage was 480 mV, short circuit photocurrent was 0.182 mA, filling factor - 0.63, efficiency - 0.232%. The authors suggest that low efficiency may be associated with the surface reflection of incident phonon heating and nonohmic contacts. Despite the low efficiency of developed solar cells, they stay perspective due to the low cost and availability of the materials.

In [15] solar cells based on Cu2O and CuO were prepared using electrodeposition. Developed structures have an efficiency of 0.25%, filling factor - 0.33, photocurrent density of short circuit - 2.7 mA/cm2 and open circuit voltage - 0.28 V. Authors associate the low conversion efficiency with a large thick of ZnO layers. It is assumed that the optimization of the thickness of the active layers can increase efficiency.

For solar cells based on Cu2O maximum efficiency of ~ 3.8% was obtained in [20], where authors used high-temperature annealing and pulsed laser deposition. Among the main ways of increasing the efficiency of solar cells based on Cu2O/ZnO and Cu2O/ZnO, the following can be identified: improving quality of material, direct doping can improve electrical properties of the oxides of copper and zinc to accumulate charge carriers; improving uniformity of layers can minimize leakage current and increase fill factor.
Among the main ways of increasing the efficiency of solar cells based on CuO/ZnO and Cu₂O/ZnO, the following can be identified [7]:

- improving the quality of material, direct alloying can improve electrical properties of the oxides of copper and zinc to accumulate charge carriers;
- increasing the area due to the fractal structure of p-n transition at the mating faces;
- improving uniformity of layers can minimize leakage current and increase fill factor.

The aim of the work was study of the processes of formation of thin film heterostructures on the basis of copper and zinc oxides by high frequency magnetron sputtering of powder targets.

II. OBTAINING OF THE STRUCTURES

Thin film ZnO/CuO heterostructures were prepared by applying zinc oxide and copper by reactive high frequency magnetron sputtering on a glass substrate. The targets for the deposition of zinc oxide films and copper oxide powders used chemically pure ZnO and analytical grade CuO. Thin films of copper were deposited by magnetron sputtering at room temperature under an argon atmosphere at a pressure of 2·10⁻⁵ bar. The substrates were placed at a distance of about 20 cm from the target. In order to control the optical properties of ZnO samples near fastened clean glass substrates. After the deposition, films were annealed in air to form a layer of copper oxide and ZnO-CuO structures. Annealing was carried out either in a muffle furnace or in a quartz furnace pulse thermal annealing.

The performed set of experiments showed that the studied oxides are characterized by low spraying speeds; were obtained relations between the growth velocity of zinc and copper oxide and the power of high frequency discharge and worked out technological spraying regimes of layers. Thin film samples of oxide structures were fabricated, which represented the following sequence of layers: glass/n-ZnO/p-CuO/Me and glass/n-ZnO/ZnO/p-CuO/Me (see Fig. 1). As electrode materials (Me) were used Cu, Pt, Ag, Ni, Al. The best results were obtained with Pt electrodes.

III. TECHNOLOGY

ZnO/CuO heterostructures were prepared by layering films of zinc oxide and copper by reactive RF magnetron sputtering at a specialized facility.

The ZnO films were prepared by chemical vapor deposition using the organometallic compounds at a low pressure. (C₂H₅)₂Zn and deionized water were used as precursors. Their concentration ratio was [H₂O]:[DEZ] = 5:6. The ZnO films were doped by boron using a gas mixture of 2% B₂H₆ in hydrogen [21], [22].

Block diagram of the equipment and its internal accessories are shown in Fig. 2, 3. The nutria vacuum chamber are two magnetron 100 mm in diameter (Fig. 3) connected to the RF generator operating at a frequency of 13.56 MHz and allows to vary the input power to the magnetron from 10 watts to 1000 watts.

The targets of ZnO and CuO powders were evenly distributed over the entire surface of the magnetrons.
Experiments have shown that the investigated oxides characterized by low spraying speeds. Dependence of the rate of growth of zinc oxide and copper on the RF discharge are shown in Fig. 4.

![Fig. 3. The inner casing of the vacuum chamber](image)

![Fig. 4. Dependence of the rate of growth of ZnO films and CuO on the power of RF discharge](image)

Basic parameters of the deposition process, oxide films are shown in the Table 1.

<table>
<thead>
<tr>
<th>The parameters of the process</th>
<th>ZnO</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power RF discharge, W</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>The composition of the gas mixture</td>
<td>76%Ar+24% O2</td>
<td>76%Ar+24% O2</td>
</tr>
<tr>
<td>The operating pressure of the gas mixture, millimeters of mercury</td>
<td>10-2</td>
<td>10-2</td>
</tr>
<tr>
<td>Substrate temperature (self-heating), °C</td>
<td>260-270</td>
<td>260-270</td>
</tr>
<tr>
<td>Film growth rate nm / min</td>
<td>1.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Spraying time, min</td>
<td>90</td>
<td>180</td>
</tr>
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</table>

In this work we use Pt, Ag, Ni, Al thin films as contacts for the CuO/ZnO heterostructures. The top electrodes were deposited on the previously formed heterostructures. A distinctive feature of the formation of the upper electrodes are reduced deposition temperature. Modes of deposition of the upper electrodes were chosen based on previous studies. The configuration of the upper electrode was created by using a shadow mask. The area of each electrode was 3.14 or 6.75 mm².

Platinum electrodes of 100 nm thickness were deposited by ion-plasma method of three-electrode type (Fig. 5). Technological parameters of the process are given in Table II. The resulting films have a surface resistance of 10 ohms.

![Fig. 5. A block diagram of ion-plasma deposition method of the three-electrode type.](image)

<table>
<thead>
<tr>
<th>TABLE II. THE MAIN PARAMETERS OF THE DEPOSITION OF Pt FILMS</th>
</tr>
</thead>
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<tr>
<td>Parameters</td>
</tr>
<tr>
<td>------------------------------------------------------------</td>
</tr>
<tr>
<td>The composition of the working gas</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Substrate temperature</td>
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<tr>
<td>Anode current</td>
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<tr>
<td>Voltage on the target</td>
</tr>
<tr>
<td>Cleaning the substrate in the plasma</td>
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<tr>
<td>Deposition time</td>
</tr>
<tr>
<td>Growth rate of the films</td>
</tr>
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</table>

Ag, Ni and Al electrodes of 100 nm thickness were deposited by electron-beam sputtering method using Mantis Qprep 500E (Fig. 6). Technological parameters of deposition process are shown in Table III. Measured by four-probe sheet resistance Ag, Ni and Al films were 1.08 ohms, 9.2 ohms and 2.7 ohms, respectively.

![Fig. 6. Equipment of QPREP 500E Mantis Deposition](image)
### Table III. The main parameters of the deposition of Ag, Ni, and Al films

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ag</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual pressure, Torr</td>
<td>5-7.10^-7</td>
<td>5-7.10^-7</td>
<td>5-7.10^-7</td>
</tr>
<tr>
<td>Substrate rotation speed, rpm</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Substrate temperature, °C</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Deposition rate, nm/ min</td>
<td>24</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>Deposition time, min</td>
<td>4</td>
<td>5</td>
<td>8.4</td>
</tr>
</tbody>
</table>

### IV. Study and Results

Investigation of electrophysical parameters of copper oxide films was carried out on the installation ECOPIA HMS-5000. Measurements showed that samples have p-type conductivity and have a high surface resistance. Also the transmittance and the reflection spectra of the films were measured. Measurements were performed on AvaSpec-2048 spectrophotometer in the visible range of 400...1000 nm using a fiber-optic module for measuring reflectance spectra. The estimations of the band gap of studied samples was 1.6...1.7 eV. Optical studies have shown that while reactive high frequency magnetron sputtering of copper oxide powder target took place, copper oxide (II) is deposited on a substrate, which is also confirmed by X-ray phase analysis data.

The reflection and the absorption spectra of CuO films showed no thermal effect up to 350 °C inclusive, that indicating stability of the formed oxide. Zinc oxide films had transmittance of about 80% in the wavelength range from 400 to 1100 nm.

Studies of current-voltage characteristics of oxide ZnO/CuO heterostructures have been carried out in dark mode and under a light source with a spectral response close to the solar spectrum. The structures with additional layer of ZnO shows better IV characteristics (see Fig. 7). This difference is explained by the fact that the layer of ZnO align energy characteristics in the band diagram (see Fig. 8). Experimental data on the characteristics of the electron transport in thin-film oxide heterojunction structures with CuO/ZnO were obtained.

![Fig. 7. I-V characteristics of a) p-CuO/n-ZnO, b) p-CuO/i-ZnO/n-ZnO](image)

![Fig. 8. Energy band structure in equilibrium of a) p-CuO/n-ZnO, b) p-CuO/i-ZnO/n-ZnO](image)
It was found that in the samples, where copper oxide was deposited at elevated temperatures up to 300 °C, characteristics differed by weak nonlinearity and of existence of a large series resistance, that was presumably a consequence of the degradation of conductive zinc oxide layer in the structure.

The samples, that were formed at low temperatures, also showed weak photoresponse and high series resistance, presumably because of not well-formed crystal structure of the films. Selection of medium temperatures (about 200...250 °C) allowed to reduce the series resistance of the structure, and adding a part of the structure of heterojunction n-ZnO/p-CuO thin intermediate layer of zinc oxide (ZnO) can improve the nonlinearity of the current-voltage characteristics and improve the photoresponse heterostructures. However, the obtained results needed further optimization.

The influence of thermal annealing in air in the temperature range up to 550 °C on the electrical properties of ZnO is investigated. It is found that electrical characteristics of the ZnO film are not changed to the annealing temperature of 200 °C, then at temperatures ranging from 200 °C to 500 °C carrier concentration and especially their mobility reduces significantly, respectively films resistance increases. The carrier concentration falls to about 10 times comparing to the initial films, mobility reduces to ∼ 0.3 cm²/(V·s). Apparently the annealing on the air reduces the concentration of oxygen vacancies and causes increase in concentration of oxygen adsorbed on the grain boundaries, which leads, firstly, to capture the free carriers at grain boundaries and, consequently, causes depletion of the volume. Secondly, the occurrence of the charge at the grain boundaries leads to high free carrier scattering.

Note, that treatment of such samples with low carrier mobility and previously annealed in the air, in vacuum at 450...500 °C results in a significant recovery of electrical properties: the mobility is restored to the original value, and the carrier concentration increases up to 25-50% of the initial value. This shows the role of oxygen in the degradation of the electrical properties of the films during annealing in the air. Therefore, to store good electrical characteristics of polycrystalline ZnO films we should avoid prolonged treatments at high temperatures.

Fig. 9 shows an optical absorption spectrum of the two films deposited on the glass substrate after annealing at 250 °C (1), and 350 °C (2) for 30 min. It is evident that after annealing at 250 °C in the absorption spectra of the two steps occur at a photon energy of 1.5 eV and 2.5eV. After annealing at 350 °C contribution of the absorption at 1.5 eV of photon energy increases significantly. This result may indicate the formation of Cu₂O (with bandgap of 2.5...2.6 eV) and CuO (with bandgap of 1.5 eV) phases, and with increasing temperature annealing the content of CuO phase increases. This conclusion is confirmed by studies of the composition of films by X-ray diffraction. Thereby, copper films annealing at temperatures 220…350 °C in the air leads to the formation of mixed phase Cu₂O and CuO, and the phase contribution depends temperature and time of the annealing.

Fig. 10 shows the current-voltage characteristics of the n-ZnO / p-CuO immediately after application of layer of copper on ZnO (1) and after pulse annealing in the air at temperatures of 250 °C (2), 350 °C (3), 450 °C (4) and 550 °C (5) for 1 minute.

It is found that the current-voltage characteristics of the samples significantly depend on the annealing temperature and duration. During thermal annealing for 10...30 minutes ohmic current-voltage characteristics were observed. However, the formation of structures using a short (1 min) pulse thermal annealing in air in the temperature range 250...550 °C reduces leakage currents and increases the magnitude of the potential barrier allows to obtain the diode current-voltage characteristics. Typical current-voltage characteristics at room
temperature as measured in the dark on the structures of about 1 mm² are shown in Fig. 10. It can be seen that the original CuO/ZnO structures demonstrate linear current-voltage characteristics. At the annealing at 250 °C for 1 minute structures acquire diode current-voltage characteristics.

Thereby, normal and pulse thermal annealing have significantly different effects on the emerging current-voltage characteristics. Note that the results obtained after rapid annealing at 250…550 °C structure of n-ZnO/p-CuO demonstrate significant photosensitivity to visible light, and while being illuminated - forward current rises several times, while the reverse current is almost unchanged. Thus, a short time annealing in air in the range of 250 °C does not cause significant degradation of the properties of ZnO thin film and lead to recieve the heterojunctions n-ZnO/p-CuO.

V. CONCLUSIONS

Thus, in this work the high frequency magnetron sputtering of zinc and copper oxide powder target was first used to form heterostructures ZnO/CuO in one vacuum cycle. Research of electrophysical and optical parameters of obtained structures was made. There are a needig in improving in the technological parameters in the manufacturing process to use similar structures in photovoltaics. The influence of thermal annealing on the electrical properties of ZnO films is obtained. Annealing of the ZnO films at temperatures above 200 °C causes the degradation of the electrical properties, the carrier concentration and mobility reduces, sheet resistance increasing. Subsequent annealing of the samples in a vacuum results in a significant recovery of electrical parameters. It is found that the method of deposition of thin layers of copper on ZnO films followed by rapid oxidation in air for 1 minute in the temperature range 250…550 °C allows to receive photosensitive thin film n-ZnO/p-CuO heterojunction.

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