Thin-film heterostructures based on oxides of copper and zinc obtained by RF magnetron sputtering in one vacuum cycle

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Abstract. Investigations of formation conditions of oxide heterostructures ZnO/CuO in the same vacuum cycle using RF magnetron sputtering of powder targets of zinc and copper oxides were carried out. The optical and electrical properties of the thin film structures were studied.

1. Introduction
Among new promising photoactive materials some oxide semiconductors such as Cu$_2$O, 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 Cu$_2$O 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 [1], relatively high coefficient of absorption spectrum of sunlight. For Cu$_2$O 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 eV [2].

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 [3–7]. For solar cells based on Cu$_2$O maximum efficiency of ~ 3.8 % was obtained in [8], where authors used high-temperature annealing and pulsed laser deposition. Among the main ways of increasing the efficiency of solar cells based on CuO/ZnO and Cu$_2$O/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.

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.

2. 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 (figure 1). As electrode materials (Me) were used Cu, Pt, Ag, Ni, Al. The best results were obtained with Pt electrodes.

![Figure 1. Schematic representation of obtained structures: (a) – p-CuO/n-ZnO; (b) – p-CuO/i-ZnO/n-ZnO.](image)

**3. Study of the obtained structures**

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 I–V characteristics (figure 2).

![Figure 2. I–V characteristics of p-CuO/n-ZnO (a) and p-CuO/i-ZnO/n-ZnO (b).](image)
This difference is explained by the fact that the layer of ZnO align energy characteristics in the band diagram (figure 3). Experimental data on the characteristics of the electron transport in thin-film oxide heterojunction structures with CuO/ZnO were obtained.

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.

![Figure 3. Energy band structure in equilibrium: (a) – p-CuO/n-ZnO; (b) – p-CuO/i-ZnO/n-ZnO.](image)

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 results need further optimization.

4. 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 is a need in improving in the technological parameters in the manufacturing process to use similar structures in photovoltaics.

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