Formation of the thin film heterostructures CuO/ZnO by RF magnetron sputtering powder targets

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Abstract. Method for forming thin film heterostructures ZnO/CuO in a single technological cycle with vacuum circuit using RF magnetron reactive sputtering of copper powder and zinc oxide was offered. The resulting film CuO had a band gap of 1.6...1.7 eV and possessed stability up to 350°C. ZnO film had a transparency of 85% in the wavelength range of 400...1100 nm. Selection of medium temperatures for forming the heterostructure (200...250°C) allowed to reduce its series resistance, and the addition of the thin heterojunction structure of the intermediate layer i-ZnO allowed to improve nonlinearity voltage characteristics and improve the photoresponse.

1. Introduction
Existing limitations of modern photovoltaic cells leads to the needs to find more efficient materials for solar cells, as well as the development of new technologies for their production [1–3]. As photoactive layer for such heterostructures considerable interest has copper oxide, as it’s absorption spectrum is consistent with the solar radiation spectrum [4]. Furthermore, copper oxide has p-type conductivity, which in combination with other oxides, such as zinc oxide films (n-type conductivity) [5–7], allows the formation of heterostructure solar cells [1]. In addition to the n-ZnO/p-CuO heterojunctions themselves, the heterostructures of zinc and copper oxides with PZT are also of interest for photovoltaic applications [8–10] due to the ferroelectric photovoltaic effect at the interface of the PZT and semiconductors [2, 10, 11].

The main methods of producing films of copper oxide or zinc oxide are reactive ion-plasma sputtering of metal targets, CVD or sol-gel methods. In this work was chosen the RF magnetron sputtering from a target of powder to produce oxide films of zinc and copper. It should be noted that the developed method allows forming heterostructure n-ZnO/p-CuO in a single technological cycle.

This paper is a continuation of studies [3, 12, 13] as development of thin film oxide layers and heterostructures for photovoltaic applications.

2. Obtaining of thin film heterostructures CuO/ZnO by RF magnetron sputtering
Heterostructures ZnO/CuO prepared layering films of zinc oxide and copper by reactive RF magnetron sputtering on a specialized installation scheme of which and its inner casing shown in figure 1. Inside the vacuum chamber are two magnetrons 100 mm (figure 1(b)), connected to the RF
generator operating at 13.56 MHz and allowing to vary the power input to the magnetron from 10 W to 1000 W.

As the target for sputtering films of zinc oxide and copper were used CuO and ZnO chemically pure powders distributed evenly across the surface of the magnetrons. Complex conducted experiments showed that the investigated oxides characterized by low sputtering rates. Dependence of growth rate of zinc oxide and copper on the RF discharge are shown in figure 2. It should be noted that a further increase in the RF power discharge to increase the film growth rates is undesirable because it will lead to overheating and eventual magnetrons failure. The thicknesses of the obtained ZnO layers were 120 nm and CuO 400 nm; optimal parameters of the films (table 1) were selected.

![Flowchart of reactive RF magnetron sputtering](a) and the inner casing of the vacuum chamber (b).

**Figure 1.** Flowchart of reactive RF magnetron sputtering (a) and the inner casing of the vacuum chamber (b).

Thus, in this work it was first used by RF magnetron sputtering zinc oxide powder target and copper oxide to form heterostructures ZnO/CuO in one vacuum cycle.

In this work as a transparent contact substrate was used a glass with the conductive layer of zinc oxide doped with boron. As the opaque contact to heterostructures ZnO/CuO used thin films Pt, Ag, Ni, Al. Top electrodes were deposited on the already formed heterostructure. A distinctive feature of forming the upper electrodes are decreased deposition temperature. Modes of obtaining top electrodes are basing on previous studies. The configuration of upper electrodes created by the use of a shadow mask. Electrode area was 3.14 and 6.75 mm².
### Table 1. Major parameters of the deposition process, oxide films.

| Process parameters                      | ZnO  | CuO  |
|-----------------------------------------|------|------|
| RF discharge power, W                   | 100  | 150  |
| The composition of the gas mixture      | 76% Ar + 24% O₂ | 76% Ar + 24% O₂ |
| The operating pressure of the gas mixture, mm Hg | 0.01 | 0.01 |
| Substrate temperature (Self-heating), °C | 260...270 | 260...270 |
| Film growth rate, nm/min                | 1.3  | 2.1  |
| Deposition time, min                    | 90   | 180  |

3. **Study optical properties of the copper and zinc films oxides**

Were measured spectra of reflection and transmission copper oxide films prepared by RF magnetron sputtering on the glass substrate. Measurements were taken on the spectrophotometer AvaSpec-2048 in the visible spectral range of 400...1000 nm using a fiber-optic module for measuring the reflection spectra. As a comparison reference for the transmission spectra measuring was used air, for measuring reflectance spectra – aluminized mirror. In the part of spectra near the wavelength 500 nm was observed intrinsic absorption edge in the region of longer wavelengths – alternating maxima and minima due to interference of the radiation reflected from the upper and lower sides of the film.

In accordance with the Lambert-Bouguer-Beer law from the reflection and transmission spectra was calculated absorption spectrum of the copper oxide. The calculation results showed that used in this work method of optical characteristics of thin films, including a parallel registration transmission and reflection spectra allows almost completely eliminate the influence of interference in the analysis of absorption spectra.

Figure 3 shows the results of studies of the copper oxide films absorption spectra. The value of the band gap width 1.6...1.7 eV corresponds to the fact that the obtained thin films are CuO. This conclusion was also confirmed by the results of X-ray analysis.

![Figure 3. The absorption spectra of copper oxide (a) and determining of the copper oxide band gap (b).](image-url)
Reflection (R) and absorption (T) spectra of films CuO showed no thermal effect to 350 °C inclusive that indicates the stability of the formed oxide, that showed in figure 4.

![Image](image1.png)

**Figure 4.** The spectra of transmission (a) and reflection (b) copper oxide without annealing and with at 150, 265, 365 and 500 °C.

Study of transmission spectra zinc oxide films have shown that they have a transparency 85 % in the wavelength range from 400 to 1100 nm.

4. **Study electrical properties of thin film heterostructures based on oxides of copper and zinc**

Investigation of the current-voltage characteristics of thin film heterostructures ZnO/CuO was carried out in the dark mode and under illumination using a light source with a spectral characteristic close to the solar spectrum. Figure 5 shows the results of research.

![Image](image2.png)

**Figure 5.** The current-voltage characteristics of heterostructures Glass/n-ZnO/p-CuO/Pt (a) and Glass/n-ZnO/i-ZnO/p-CuO/Pt (b) by dark mode (1) and under illumination (2).

Has been found that in the samples where the copper oxide applied at higher temperatures up to 300 °C, the characteristics were weak nonlinearity and had large series resistance, that was presumably a consequence of the diffusion of boron in the structure. Samples which were formed at low temperatures exhibited weak photoresponse and high series resistance, presumably due to imperfectly formed crystalline structure of the films. Selection of medium temperature (about 200...250 °C) allows to reduce the series resistance of the structure. Adding a thin intermediate layer of zinc oxide (i-ZnO) in heterostructure n-ZnO/p-CuO improved the nonlinearity of the current-voltage characteristics and the photoresponse of heterostructures.
5. Conclusions
A new technology of forming heterostructures n-ZnO/p-CuO in a single process cycle with using RF magnetron reactive sputtering of copper and zinc oxide powder targets. The obtained copper oxide films had a band gap 1.6...1.7 eV and possessed stability during heat treatment to 350 °C. Zinc oxide film had a transparency 85 % in the wavelength range from 400 to 1100 nm. Were obtained the first thin film oxide structure samples with the following sequence of layers: Glass/n-ZnO/i-ZnO/p-CuO/Me. As electrode materials (Me) were used Cu, Pt, Ag, Ni, Al, but the best results were obtained using Pt. Selection of medium temperature (about 200...250 °C) allows to reduce the series resistance of the structure. Thin intermediate layer of zinc oxide (i-ZnO) improve the nonlinearity of the current-voltage characteristics and improve the photoresponse heterostructures. However, there are the field for future research.

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