Investigation of photoelectric properties of CuO / PZT heterostructures in the visible and near IR regions

K.V. Kochunov, G.A. Konoplev, N.D. Mukhin, D.A. Chigirev
Saint-Petersburg Electrotechnical University, 197376, Saint-Petersburg, Russia
E-mail: kochunovk@mail.ru

Abstract. The method of formation of copper oxide / lead zirconate titanate (CuO/PZT) heterostructures using RF magnetron sputtering of chemically pure grade copper oxide powder on prepolarized ferroelectric ceramic substrate is considered; the direction of polarization was parallel with the copper oxide film plane. The short-circuit photocurrent in the CuO/PZT samples with different thicknesses under irradiation in the visible and near IR regions was measured. The spectral dependences of the photocurrent were estimated. The maximum photoresponse of the structures was observed at the wavelength of 515 nm.

1. Introduction
The possibilities of creating solar cells based on ferroelectric materials are actively discussed in the scientific literature. Of particular interest are the photoelectric properties of ferroelectric / semiconductor heterostructures. Thus, solar cells based on PZT/ZnO [1] and PZT/CuO [2] heterocontacts were demonstrated. The ferroelectric/semiconductor heterostructures with lead-free oxide perovskites, such as barium titanates [3] and strontium titanates [4], are also being studied.

In the present work authors studied the photoelectric properties of CuO/PZT heterostructures including the spectral dependences of the short circuit photocurrent under irradiation in the visible and near IR regions. This paper is a continuation study of works [5-7] as development of thin film oxide layers and heterostructures technology for photovoltaic applications.

2. Formation of thin film CuO/PZT heterostructures by RF magnetron sputtering
Ferroelectric / semiconductor (CuO/PZT) heterostructures were fabricated by reactive RF magnetron sputtering of copper oxide (CuO) thin film on ferroelectric lead zirconate titanate (PZT) ceramic substrate; the direction of polarization was parallel with the CuO film plane. Planar electrodes (Al) with the 0.5 mm gap were deposited on the top of the oxide layer (figure 1).

![Figure 1. Schematic representation of the studied samples.](image)

The sputtering machine with the 100 mm magnetron inside the vacuum chamber was used; the magnetron was connected to the RF generator capable of the input power variation from 10 W to 1000...
W. The sputtering target was chemically pure grade copper oxide powder evenly distributed over the entire surface of the magnetron. Main parameters of the deposition process: RF discharge power - 150 W, the composition of the gas mixture - 76% Ar + 24% O₂, substrate temperature - 260…270 ºC. The operating pressure of the gas mixture and the deposition time were varied (table 1) to produce samples with different thickness of CuO layer (from 50 to 100 nm).

| #  | The operating pressure, mmHg | Deposition time, min | Film thickness, nm |
|----|-----------------------------|----------------------|-------------------|
| 1  | 0,01                        | 30                   | 50                |
| 2  | 0,01                        | 60                   | 100               |
| 3  | 0,025                       | 30                   | 50                |
| 4  | 0,025                       | 60                   | 100               |

3. Investigation of photoelectric properties of CuO / PZT heterostructures

Keithley 6487 Picoammeter was used to research the photoelectric properties of the structures. All samples were irradiated with an ultra-bright LED with a wavelength of 515 nm, which is close to the central wavelength of the solar spectrum. The short-circuit photocurrent was measured. The LED was located at a distance of 10 mm from the sample and powered with rectangular pulses of 50 mA current.

The photocurrent Iₚₕ was calculated as the difference between the short-circuit current I at the time of turning on the LED and the dark current Iₖ at the time of turning off the LED:

\[ I_{ph} = I - I_d. \]

The results of the experiments showed that the sample # 4 (figure 2) produced the highest value of the short-circuit photocurrent (table 2).

| #  | Iₚₕ, pA |
|----|---------|
| 1  | 1,8     |
| 2  | 2,3     |
| 3  | 2       |
| 4  | 2,5     |

This can be explained by the fact that this sample had thicker CuO films; therefore, a larger portion of the incident optical radiation was absorbed.

Figure 2. The short-circuit photocurrent for sample # 4 under irradiation at the wavelength of 515 nm (“ON” - LED is turned on, “OFF” - LED is switched off).

Then, sample # 4 was irradiated with ARLight LEDs at various wavelengths (400 nm, 470 nm, 515 nm, 630 nm, 940 nm; figure 3). The operating currents of all LEDs were adjusted in such a way as to produce equal photon flux density upon the surface of the sample at different wavelengths. On the basis of the obtained result we estimated the spectral dependence of the short-circuit photocurrent for
sample # 4 (figure 4). The maximum photoresponse was observed at 515 nm. The decrease in photosensitivity in the shorter wavelength region is most likely caused by an increase in the absorption of radiation near the upper surface of the CuO film and the growing influence of surface recombination. In the long-wavelength region of photosensitivity gradually decreases with a decrease in the absorption of the film. In the IR region at a wavelength of 940 nm, the response is practically not observed, which makes it possible to exclude the influence of the pyroelectric effect in PZT.

A decrease in the photocurrent during prolonged irradiation may be explained by long-time relaxation processes caused by high defect density in the CuO layer. The effect depends on the level of irradiation and is more pronounced for particular samples. Detailed explanation of this phenomenon requires further research.

![Figure 3](image3.png)

**Figure 3.** The short-circuit photocurrent for sample # 4 under irradiation at the wavelength of 400, 470, 515, 630 and 940 nm.

![Figure 4](image4.png)

**Figure 4.** Spectral dependence of the short circuit photocurrent for sample # 4.

4. **Conclusions.**

It was proved that copper oxide/lead zirconate titanate CuO/PZT heterostructures fabricated using RF magnetron sputtering of copper oxide thin film on ferroelectric prepolarized lead zirconate titanate ceramic substrate (the direction of polarization is parallel with the copper oxide film plane) show
photoelectric response under optical irradiation in the visible region. The spectral dependences of the short-circuit photocurrent were estimated and the maximum photoresponse was observed for the sample with 100 nm CuO layer at the wavelength of 515 nm which is close to the central wavelength of the solar spectrum. It can be concluded that such heterostructures have great potential for photovoltaic applications but there are the field for future research.

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