Electrical Properties of *p*-$CuCoO_2$/*n*-Si Heterojunction

D. P. Koziarskyi, I. P. Koziarskyi, and E. V. Maistruk

Abstract *p*-$CuCoO_2$/*n*-Si heterostructures were produced by radio frequency magnetron sputtering of $CuCoO_2$ thin films on *n*-Si crystalline substrates. The optical properties of $CuCoO_2$ thin films deposited on glass substrates are studied. The mechanisms of current transfer are analyzed based on temperature dependences of *I–V* characteristics. The influence of light on the electrical properties of the *p*-$CuCoO_2$/*n*-Si heterostructure is determined.

1 Introduction

$CuCoO_2$ belongs to the group of delafossites, which are known for a wide range of electrical properties. The conductivity of these compounds can vary from insulating to metallic materials. $CuCoO_2$ has found applications such as catalyst for oxygen evolution reaction [1], as thermoelectric materials [2] and as absorber materials [3].

Since these compounds simultaneously have a fairly good transparency to visible light and high electrical conductivity, they can be attributed to the group of transparent conductive oxides (TCO). TCO thin films are widely used as transparent electrodes in photoelectronic and lighting devices [4]. p-type TCOs give us the opportunity to manufacture transparent p–n heterojunctions, diodes and transistors, so their further research is quite promising [5, 6]. Since delafossite oxides have p-type semiconductor properties and fairly high optical transparency for visible light, they can be used for this purpose.

$CuCoO_2$ thin films are fabricated by using different deposition techniques such as sol–gel method [1, 3], ion exchange [2], RF magnetron sputtering [7], conventional solid-state reaction method [8] and low-temperature hydrothermal synthesis [9]. However, it is known that vacuum sputtering processes are more suitable for obtaining films of higher quality.

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Therefore, the fabrication of the p-$CuCoO_2$/n-Si heterostructure by radio frequency magnetron sputtering of $CuCoO_2$ thin films on n-Si crystalline substrates is of certain scientific interest.

2 Experiment Details

Thin films of $CuCoO_2$ (thickness ~200 nm) were deposited on glass substrates (for optical studies) and on plane-parallel n-Si plates (for obtaining heterostructures) by radio frequency magnetron sputtering. The target for sputtering $CuCoO_2$ films was made from a stoichiometric mixture of CuO and CoO_2, which was pressed into a special aluminum cup. The aluminum cup has such a shape that the plasma does not interact with its material. The radio frequency magnetron sputtering system is installed in the UVN-70 universal vacuum unit. Deposition was carried out in an atmosphere of inert gas (argon) and at a magnetron frequency of 13.56 MHz. To obtain a high vacuum, a TMN-500 turbomolecular pump was used [10]. Substrate temperature $T_S = 653$ K, spraying was carried out in two stages $t_1 = 15$ min, $P_1 =$ 180 W, $t_2 = 15$ min, $P_2 = 200$ W (t—spraying time, P—magnetron power).

The thickness of the films was determined by applying them to a sital substrate and then scribing and studying the interference pattern obtained with the Linnik MII-4 microinterferometer.

To carry out optical studies, thin films of $CuCoO_2$ were applied to the cover glass and the optical transmission spectrum was recorded using a spectrophotometer SF-2000 in the wavelength range of incident radiation $\lambda = 0.2–1.1$ μm [11].

The four-probe method was used to determine the surface resistance of films ($\rho_\square = 1$ MΩ/□) [12]. Considering the thickness of the film (200 nm), the specific resistance was $\rho = 20$ Ω·cm. Silver-based conductive paste was used as ohmic contacts to $CuCoO_2$ films and n-Si substrates.

A hardware and software complex based on Arduino, an Agilent 34410A digital multimeter and a Siglent SPD3303X programmable power source were used to measure the $I–V$ characteristics of p-$CuCoO_2$/n-Si heterostructures. This complex was controlled by a personal computer using the software created by the authors in the LabVIEW environment.

An integrated light source with an illumination power density of 80 mW/cm^2 and close to AM1.5 was used to measure light $I–V$ characteristics.

3 Results and Discussion

looseness-1The absorption coefficient of $CuCoO_2$ thin films was determined using the method of independent measurement of transmission and reflection coefficients. For Cu–CoO_2 films in the studied spectrum region, the light reflection coefficient is

$R \approx 20\%$. To calculate the coefficient of optical absorption of light α, we used the formula [10, 11]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right]. \quad (1)$$

The energy and type of optical transition of an electron from the valence band to the conduction band was determined from the analysis of the absorption coefficient using the expression for semiconductors:

$$\alpha = \frac{a_0\left(h\nu - E_g\right)^n}{h\nu}, \quad (2)$$

where a_0 is a constant and n is determined by the type of optical transition of an electron from the valence band to the conduction band. To determine the type of optical transitions in thin $CuCoO_2$ films, the dependences $(\alpha h\nu)^x = f(h\nu)$ were constructed, where the values of x depend on different values of n.

The presence of a rectilinear region near the region of the own absorption edge on the spectral dependence $(\alpha h\nu)^2 = f(h\nu)$ for the $CuCoO_2$ film (Fig. 1) confirms the fact that the process of absorption of light photons occurs with the help of direct optical transitions ($n = ½$).

By extrapolating a straight section to the energy axis (Fig. 1), the optical band gap for the investigated films was determined, which was $E_g = 3.5$ eV. This value of energy for direct allowed optical transitions is in good agreement with literature data [8].

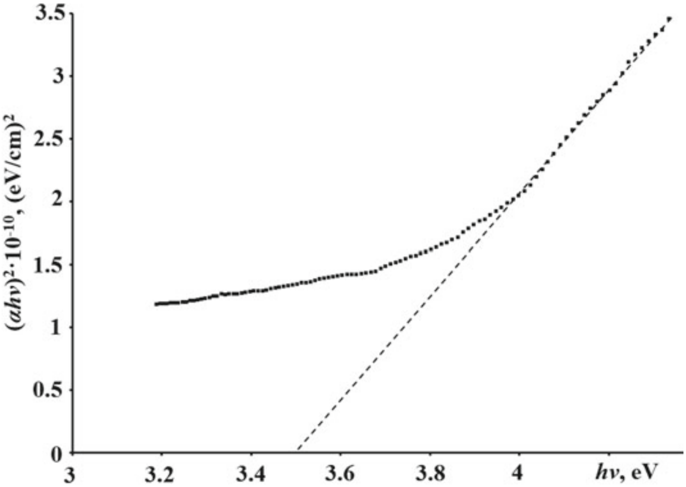


Fig. 1 Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $CuCoO_2$ films

From the *I*–*V*-characteristics of the *p*-$CuCoO_2$/*n*-Si heterostructures presented in Fig. 2, it is seen that in the temperature range $T = 299$–343 K, these heterostructures have rectifying properties. The current rectification ratio is determined at $T = 294$ K and voltages $|V| = 0.7$. *V* is equal to RR ~ 10^3.

To estimate the height of the potential barrier $q\varphi_k$, we extrapolated the linear sections of the *I*–*V* characteristics in the region of forward biases to the voltage axis. The height of the *p*-$CuCoO_2$/*n*-Si heterojunction potential barrier determined in this way at room temperature is equal to $q\varphi_k \approx 0.53$ eV. Figure 3 shows the value of the height of the potential barrier at different temperatures.

Figure 3 shows that the height of the potential barrier decreases linearly from 0.53 to 0.46 eV with increasing temperature from $T = 299$ to 343 K. Such a change in the height of the potential barrier with temperature is described by the equation:

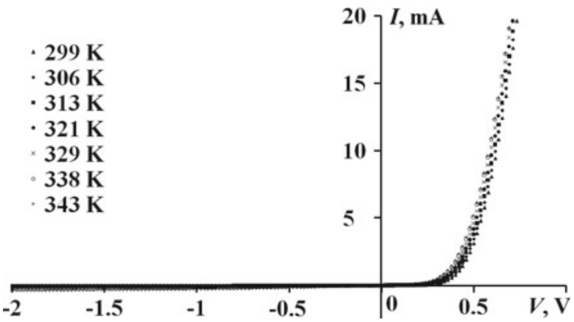


Fig. 2 *I*–*V* characteristics of the heterostructure of *p*-$CuCoO_2$/*n*-Si in the temperature range from 299 to 343 K

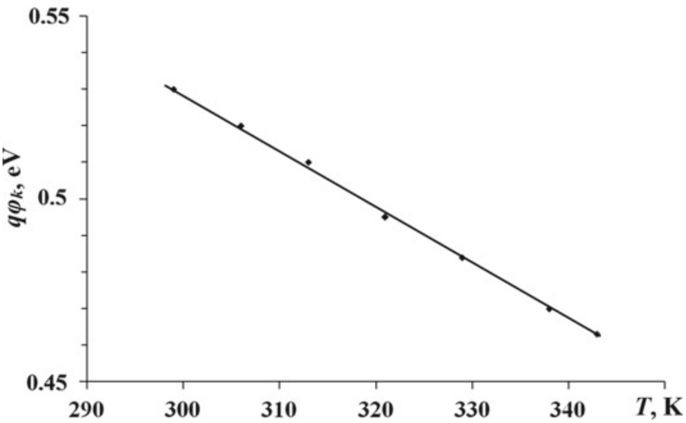


Fig. 3 Temperature dependence of the height of the potential barrier of the *p*-$CuCoO_2$/*n*-Si heterostructure

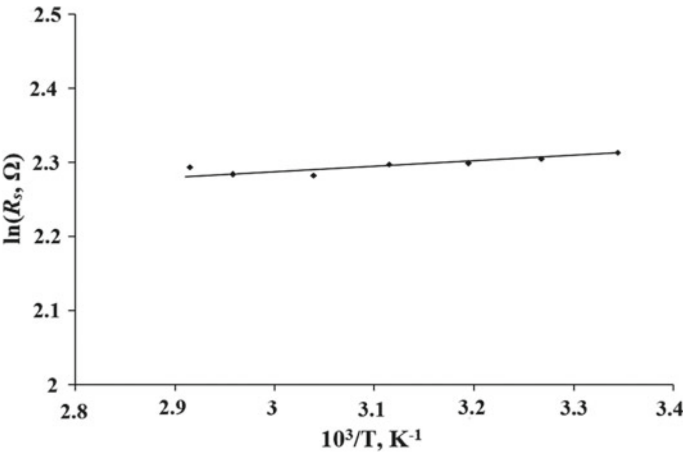


Fig. 4 Temperature dependence of the series resistance of the p-$CuCoO_2$/n-Si heterostructure

$$q\phi_k(T) = q\phi_k(0) - \beta_\phi T. \quad (3)$$

Using expression (3) and Fig. 3, the temperature coefficients of change of the height of the potential barrier and its height at 0 K were determined, which are equal to $d(q\varphi_k)/dT = -1.54 \cdot 10^{-3}$ eV/K and $q\varphi_k(0\ K) = 0.99$ eV, respectively.

The temperature dependence of the series resistance is shown in Fig. 4. From the slope of the temperature dependence, $\ln(R_s) = f(10^3/T)$ determined the depth of the donor level which is $E_d = 0{,}07$ eV, near the bottom of the conduction zone of the base material.

The mechanisms of current transfer through the p-$CuCoO_2$/n-Si heterojunction at forward biases were determined from the analysis of I–V characteristics in the coordinates $\ln I = f(V)$ (Fig. 5).

From the straight-line sections on the dependence $\ln I = f(V)$ (Fig. 5) by the tangents of their angles of inclination to the voltage axis, the non-ideality factors of heterojunctions n at different temperatures were determined (Fig. 6).

From Fig. 6, it can be seen that at small forward biases of $0.05\ V < V < 0.4\ V$, the non-ideality factor, determined from the slope of the linear dependences $\ln I = f(V)$ to the voltage axis, was $n \approx 2.1$–2.3, which indicates predominance of the generation-recombination mechanism of current transfer. At higher forward bias voltages of $0.4\ V < V < 0.6\ V$, the value of the non-ideality factor $n \approx 3.5$–4.5 (Fig. 6) indicates the predominance of the tunnel mechanism of current transfer.

As can be seen from Fig. 6, the coefficient of non-ideality depends weakly on temperature, which is typical for tunneling mechanisms of forward current generation involving surface states at the interface and defects in the space charge region, and is described by the expression [13]:

$$I(V) = B \cdot \exp(\beta T) \cdot \exp(\alpha V), \quad (4)$$

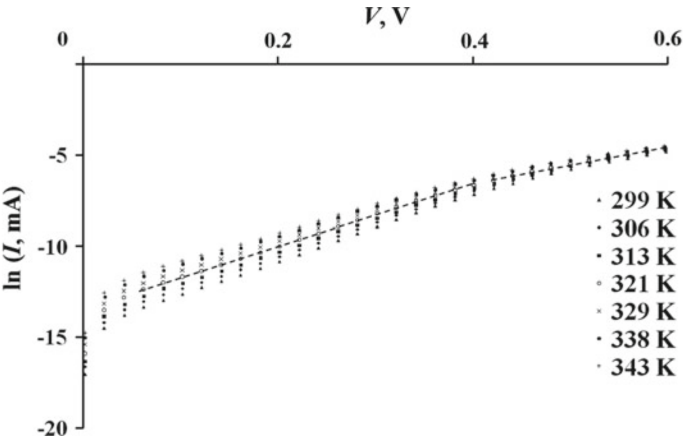


Fig. 5 Dependences $\ln I = f(V)$ at forward biases applied to the p-$CuCoO_2$/n-Si heterostructure at different temperatures

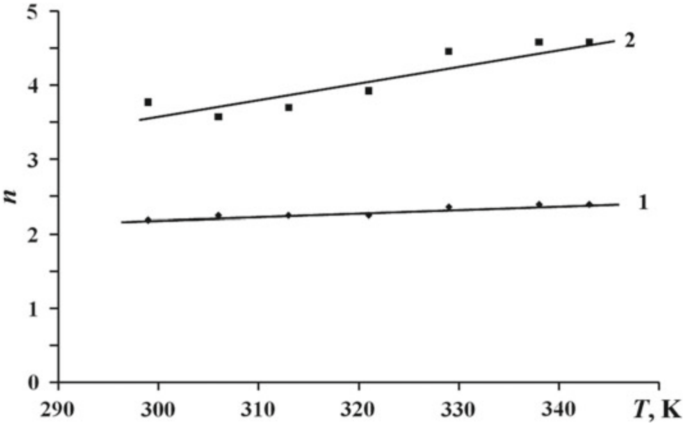


Fig. 6 Temperature dependence of the non-ideality factor at forward biases applied to the p-$CuCoO_2$/n-Si heterostructure: 1—(0.05 V < V < 0.4 V); 2—(0.4 V < V < 0.6 V)

where B, β and α are constants.

To analyze the mechanisms of current transfer at reverse biases for the p-$CuCoO_2$/n-Si heterostructure, an expression was used that describes the process of tunneling of charge carriers with the participation of surface states: The reverse branches of the I–V characteristics of the p-$CuCoO_2$/n-Si heterostructure at temperatures T = 299–343 K in the voltage range from -2 V < V < $-3kT/q$ are described by the expression for tunneling current involving surface states:

$$I_{\text{rev}}^{t} \approx a_0 \exp\left(\frac{b_0}{\sqrt{\phi_k(T) - qV}}\right), \tag{5}$$

where a_0 and b_0 are parameters that are voltage independent.

From Fig. 7, it can be seen that at the reverse biases $-2\ V < V < -3kT/q$, the I–V characteristics in the coordinates $\ln(I_{rev}) = f(\varphi_k - qV)^{-1/2}$ have a linear character. This indicates the dominance of the tunneling mechanism of current transfer with the involvement of surface states through the p-$CuCoO_2$/n-Si heterojunction.

The I–V characteristics of the studied p-$CuCoO_2$/n-Si structures, which were measured at room temperature $T = 294$ K and under integral illumination under standard lighting conditions close to AM1.5 with an illumination power density of 80 mW/cm^2, are presented in Fig. 8.

From Fig. 8, it can be seen that p-$CuCoO_2$/n-Si heterostructures have a low photosensitivity at reverse bias.

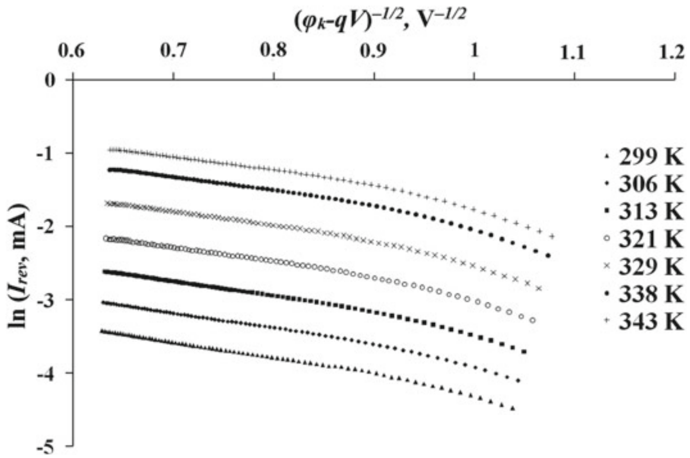
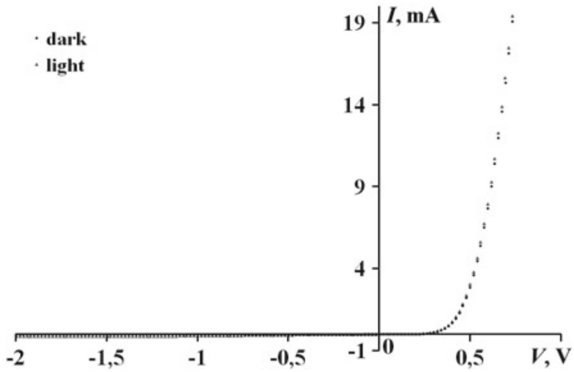


Fig. 7 Temperature dependences of reverse I–V characteristics for p-$CuCoO_2$/n-Si heterostructure

Fig. 8 Light I–V-characteristics of the heterojunction p-$CuCoO_2$/n-Si



4 Conclusion

Thin $CuCoO_2$ films (~200 nm thick) were applied to glass substrates and plane-parallel *n*-Si plates by RF magnetron sputtering. The resistivity of the $CuCoO_2$ films was $\rho = 20\ \Omega\cdot$cm at $T = 300$ K. From the analysis of the absorption spectra of $CuCoO_2$ films, it was established that these films are direct band with the optical band gap $E_g = 3.5$ eV.

The *p*-$CuCoO_2$/*n*-Si heterostructure has rectifying properties. The current rectification ratio is equal to RR ~ 10^3. The presence of an energy barrier $q\varphi_k \approx 0.5$ eV on the *n*-Si side explains the diode characteristics of the heterostructure. In the *p*-$CuCoO_2$/*n*-Si structure, at forward biases of 0.05 V < V < 0.4 V, the generation-recombination mechanism of current transfer is dominant. When the forward bias voltage increases $V > 0.4$ V, the tunneling mechanisms of current transfer with the participation of surface states dominate. At reverse biases of $-$ 2 V < V < $-$ 3*kT/q* V, the tunneling mechanisms of current transfer with the participation of surface states also dominate.

The *p*-$CuCoO_2$/*n*-Si heterostructure has a low photosensitivity at reverse bias under AM1.5 radiation conditions.

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