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Optical Properties of $CuNiO_2$ Thin Films

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The conditions of the radio frequency magnetron sputtering production of thin $CuNiO_2$ films on glass substrates have been studied. The spectral dependences of the transmission and absorption coefficients, depending on the sputtering mode, are analyzed. The optical width of the band gap for the obtained thin films is determined. The thickness of the obtained films and their resistivity were determined.

topics: thin film, $CuNiO_2$, RF magnetron sputtering, optical properties

1. Introduction

Delafossite ($CuNiO_2$), along with other minerals of its group, is known for its wide range of electrical properties. Its conductivity can vary from insulating to metallic materials. $CuNiO_2$, as well as other delafossites, have good photocatalytic properties and can possibly be used to reduce water in a solar water-splitting device [1].

$Cu_xNi_{1-x}O$ thin films can be obtained by various methods: pyrolysis, sol–gel, electrodeposition, pulsed laser deposition, pulsed plasma deposition, thermal evaporation, DC magnetron sputtering, and RF magnetron sputtering [2, 3]. Copper–nickel oxides in a thin film form are used as NO_2 gas sensor, anode for fuel cells, selective coating, solar cell, electrochromic devices, LEDs, photodiodes, p-type gate in heterojunction field-effect transistors, p-type transparent conductive coatings, antifungal coatings, and supercapacitor coatings [4–6].

However, vacuum-based sputtering processes produce higher quality films. That's why it was interesting to investigate the effect of the RF magnetron sputtering mode on the optical properties of $CuNiO_2$ thin films.

2. Experimental details

$Cu_xNi_{1-x}O$ thin films were obtained by RF magnetron sputtering on glass substrates. A stoichiometric mixture of CuO and NiO was used to make the target. This mixture was pressed into a special aluminum cup, the shape of which is chosen so that the plasma does not interact with the material of the cup. Spraying was carried out in a universal vacuum unit UVN-70 and the deposition process was in an atmosphere of inert gas, i.e., argon. The operating frequency of the magnetron was 13.56 MHz. In order to obtain a film without impurities, a turbomolecular pump TMN-500 was used [7]. Parameters of spraying process, i.e., substrate temperature, power of magnetron, and spraying time are given in Table I.

TABLE I

Parameters of the sputtering process.

Substrate temperature [°C]	Magnetron power [W]	Spraying time [min]
250	180	30
300	180	30
350	180	30
400	180	30
450	180	20

Before spraying at substrate temperatures of 300°C, 350°C, and 400°C, the target was re-pressed. At substrate temperatures of 250°C and 450°C, spraying was performed from the untreated (after the previous spraying process) target (Fig. 1).

The linnik microinterferometer MII-4 was used to determine the thickness of delafossite films. In order to obtain a good interference pattern, the film was applied to the sital substrates and scribed.

The studies of the optical transmission spectrum of thin $CuNiO_2$ films were carried out on the SF-2000 spectrophotometer in the wavelength range of incident radiation of $\lambda = 0.2$–1.1 μm [8]. As substrates for film application, the cover glass was used for the optical studies.

The surface resistance of $CuNiO_2$ films was studied using the four-probe method [9].

3. Results and discussion

The results of measurements of the resistivity of $Cu_xNi_{1-x}O$ films sprayed at different modes and their thickness are presented in Table II.

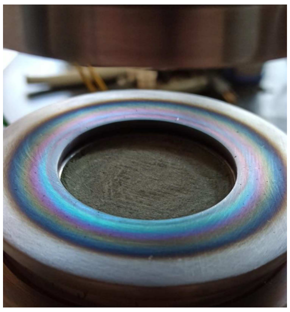

Fig. 1. Target of stoichiometric mixture of CuO and NiO after spraying process.

TABLE II

Resistivity of $Cu_xNi_{1-x}O$ films sprayed at different modes.

Substrate temperature [°C]	Surface resistance [Ω/□]	Resistivity [Ω cm]	Thicknes [nm]
250	$> 10^6$	> 15	150
300	13×10^3	0.2	150
350	$> 10^6$	> 20	200
400	$> 10^6$	> 15	150
450	25	0.00025	100

Table II shows that the films sprayed at the substrate temperature of 300°C and 450°C have good conductive properties. The conductivity of films sprayed at 450°C is more typical for metals, and at 300°C it is typical for semiconductors.

The dependence of the transmittance for $Cu_xNi_{1-x}O$ thin films applied by RF magnetron sputtering on the wavelength of the incident radiation is shown in Fig. 2.

As can be seen in Fig. 2 for the obtained films, the transmission coefficient in the wavelength range $\lambda = 0.5$–1.1 μm takes the value of $T \sim 90\%$ for thin films deposited on a substrate with the temperature of 250°C. In the region of wavelengths $\lambda < 0.5$ μm, a sharp decrease in the transmission coefficient is observed due to the intrinsic absorption edge of this film.

The dependences of the transmittance for the films applied to the substrates heated to the temperature of 300–400°C have subtle character and gradually increase with increasing wavelength to the value of $T \sim 50\%$ (Fig. 2).

The films obtained at a substrate temperature of 450°C have a low transmittance $T \sim 5\%$ (Fig. 2). Given also the high conductivity of these films (Table II), we can assume that a metal film was obtained. Therefore, at such high temperatures in this mode of spraying, almost no oxygen is deposited on the substrate.

Therefore, taking into account the dependences of the transmittance (Fig. 2) and the resistivity (Table II) of thin films, only at a substrate temperature of about 300°C a film was obtained, corresponding to transparent conductive oxides (TCO).

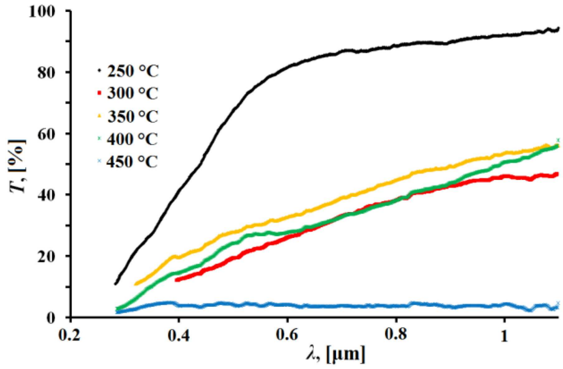

Fig. 2. The spectral dependences of the transmittance for $Cu_xNi_{1-x}O$ films deposited on substrates with different temperatures.

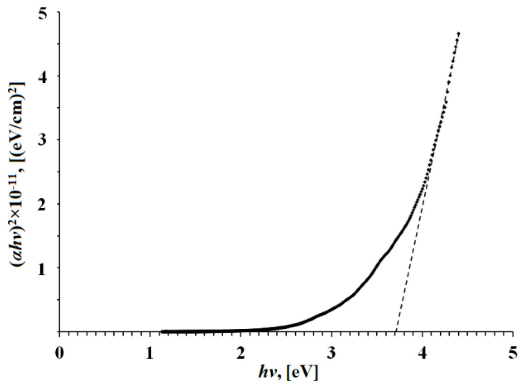

Fig. 3. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $Cu_xNi_{1-x}O$ films ($t_S^{\circ} = 250$°C, $t = 30$ min, $P = 180$ W.

The method of independent measurement of transmission and reflection coefficients was used to determine the absorption coefficient of $Cu_xNi_{1-x}O$ thin films. The light reflection coefficient R in the studied region of the spectrum for thin films of delafossites is $R \approx 20\%$. The optical light absorption coefficient α for $Cu_xNi_{1-x}O$ films was calculated by the formula [10]

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

In order to determine the energy and the type of optical transition of the electron from the valence band to the conduction band, an analysis of the absorption coefficient was performed using the expression for semiconductors [11]

$$\alpha = \frac{\alpha_0 \left(h\nu - E_g\right)^n}{h\nu}, \quad (2)$$

where α_0 is a constant, n is determined by the type of optical transition of an electron from the valence band to the conduction band. Therefore, it is necessary to construct the dependency $(\alpha h\nu)^x = f(h\nu)$, where the value of x depends on different values of n, which correspond to different types of optical transitions.

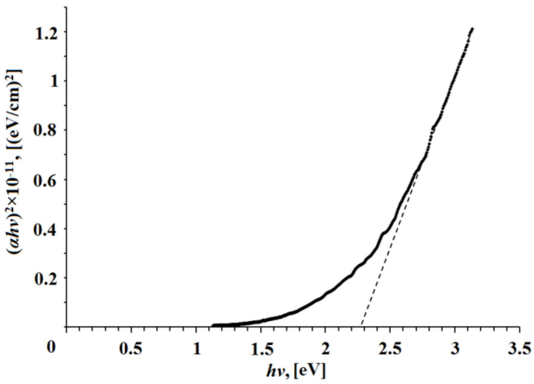

Fig. 4. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $CuNiO_2$ films (t_S° = 300°C, t = 30 min, P = 180 W.

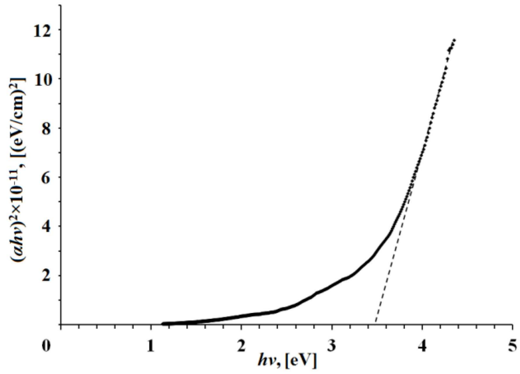

Fig. 6. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $Cu_xNi_{1-x}O$ films (t_S° = 400°C, t = 30 min, P = 180 W.

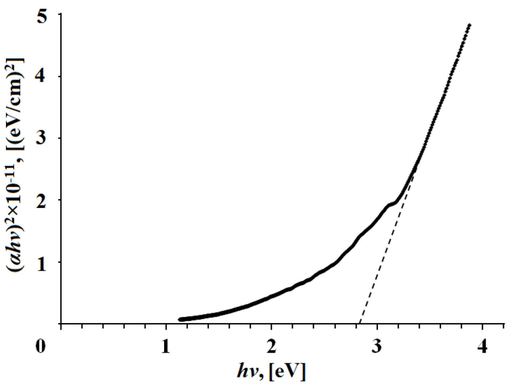

Fig. 5. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $Cu_xNi_{1-x}O$ films (t_S° = 350°C, t = 30 min, P = 180 W.

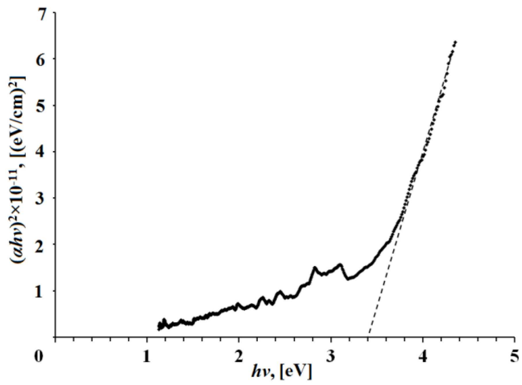

Fig. 7. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2 = f(h\nu)$ of $Cu_xNi_{1-x}O$ films (t_S° = 450°C, t = 20 min, P = 180 W.

In Figs. 3–7, the spectral dependence $(\alpha h\nu)^2 = f(h\nu)$ for the $Cu_xNi_{1-x}O$ films are shown. The presence of a rectilinear region near the region of intrinsic absorption edge on the obtained dependences confirms the fact that the process of absorption of light photons takes place by means of direct optical transitions ($n = \frac{1}{2}$).

For the studied films, the optical width of the band gap was determined by extrapolating the rectilinear sections to the energy axis. As a result, we obtained the value E_g = 3.71 eV for $Cu_xNi_{1-x}O$ thin films deposited on a substrate at the temperature of 250°C (Fig. 3). This value of the optical band gap is characteristic of the NiO films [12], which is confirmed by fairly high resistivity of these films (Table II) [13]. This can be explained by the presence of the untreated target (Fig. 1) a layer of metallic Ni on the surface. Therefore, in order to obtain high-quality films, it is necessary to clean (re-press) the target before each spraying.

The value of the optical band gap for the films sprayed at a substrate temperature of 300°C was E_g = 2.29 eV (Fig. 4). Such value of the optical band gap is characteristic of $CuNiO_2$ thin films ($x = 0.5$) [6, 14]. Given the specific conductivity and transmission of these films, this spray mode can be considered optimal for obtaining TCO of $CuNiO_2$ films.

The value of the optical band gap for films sprayed at a substrate temperature of 350°C was E_g = 2.81 eV (Fig. 5). Such value of the optical band gap is characteristic of $Cu_xNi_{1-x}O$ thin films ($x < 0.5$) [6]. However, compared to the previous mode, these films have quite high-impedance, so they cannot be attributed to TCO.

The value of the optical band gap for films sprayed at a substrate temperature of 400°C was E_g = 3.22 eV (Fig. 6). Such value of the optical band gap is also characteristic of $Cu_xNi_{1-x}O$ thin films ($x < 0.5$) [6]. An increase in the optical band gap with an increase in the substrate temperature in the range of 300–400°C can be explained by a decrease in the copper content in the resulting thin film [6].

The value of the optical band gap for the films sprayed at a substrate temperature of 450°C was E_g = 3.2 eV (Fig. 7). Given the metallic conductivity and the value of the transmittance of these films, it is likely that a translucent metal film covered with a thin layer of oxide was obtained. Given that the spraying was carried out from an untreated target, the resulting film is Ni–NiO.

Therefore, at higher temperatures (350–450°C) in this mode of spraying (RF magnetron sputtering, $P = 180$ W) using the target (stoichiometric mixture of CuO and NiO), copper will be worse deposited on the substrate than nickel.

4. Conclusions

Thin $Cu_xNi_{1-x}O$ films ($\sim$ 100–200 nm thick) were applied to glass substrates by RF magnetron sputtering at different substrate temperatures. $Cu_xNi_{1-x}O$ films have a transmittance $T \approx 5$–90% in the wavelength range $\lambda = 0.5$–1.1 μm. Analysis of the absorption spectra of the films indicates direct optical transitions. The optical band gaps of the obtained $Cu_xNi_{1-x}O$ films are $E_g = 2.3$–3.7 eV. The resistivity of the films at room temperature is $\rho = 0.0025$–20 Ω cm.

The best mode of the deposition process is a substrate temperature near 300°C. The resulting $CuNiO_2$ films have parameters close to TCO ($T \approx 50\%$, $\rho = 0.2$ Ω cm).

Before each deposition process, it is necessary to clear (re-press) the target (stoichiometric mixture of CuO and NiO).

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