Proceedings of the 50th International School & Conference on the Physics of Semiconductors

Optical and Electrical Properties of CuO Thin Films by Spray Pyrolysis Method

S.I. Kuryshchuk[a,*], I.G. Orletskii[a], O.V. Shyrokov[b], D.V. Myroniuk[b] and M.M. Solovan[a]

[a] *Department of Electronics and Power Engineering, Yuriy Fedkovych Chernivtsi National University, 2 Kotsubynsky st., 58002 Chernivtsi, Ukraine*
[b] *Institute for Problems of Materials Science of the National Academy of Sciences of Ukraine, 3 Krhyzhanovsky st., 03142 Kyiv, Ukraine*

Doi: 10.12693/APhysPolA.142.625 *e-mail: kuryshchuk.serhii@chnu.edu.ua

Thin films (300 nm thick) of CuO of p-type conductivity were precipitated using the spray pyrolysis method from 0.2 M of aqueous $CuCl_2 \cdot 2H_2O$ salt solution on preheated (up to 350°C) glass and sitall substrates. The structure and electrical and optical properties of the films are analyzed. The grain size of CuO thin films (24 nm) was calculated using the XRD analysis. The activation energy equals $E_a = 0.27$ eV, which may indicate that the conduction is due to the transition of charge carriers from the valence band to the working acceptor level. From the spectral dependence $(\alpha h\nu)^2 = f(h\nu)$ of CuO thin films, the band gap width $E_g = 1.46$ eV was determined.

topics: CuO, spray pyrolysis, optical properties, thin films

1. Introduction

The use of a variety of materials with the necessary physical, electrical, and optical characteristics is required to create and develop modern electronic devices. That is why scientists are intensively studying new and already-known chemical compounds that may exhibit semiconductor properties. Among such compounds, metal oxides can be considered the most promising [1–5].

These materials have several advantages over the majority of other compounds in the design of detectors, sensors, and photovoltaic devices. These advantages include environmental safety, non-toxicity, and chemical stability. The composition of oxides, as a rule, includes elements common in the earth's crust; the methods of obtaining the oxides are simple and require only low-temperature processing of the material. In addition, the oxide compounds themselves have the potential to be less expensive due to low-cost components and efficient and low-cost production methods [6–8].

In recent years, thin films of copper oxide (CuO) have gained great interest due to their application in many technological fields. This is due, firstly, to the low cost, non-toxicity, and widespread of copper in nature, and secondly, to copper's simple deposition. The most common and stable phases of this semiconductor are CuO (tenorite) and Cu_2O (cuprite) [9–11].

CuO is a p-type semiconductor, which, according to various data, has a band gap from 1.2 to 2.1 eV, a high absorption coefficient (10^5 cm^{-1}, 300 K), good thermal conductivity (76.5 W mK^{-1}), and electrical resistance, which can range from 10 to 10^5 Ω cm depending on the method of production [12, 13].

Copper oxides have a wide range of applications, such as solar energy conversion, optoelectronics, solar panels, gas sensors, optical switches, semiconductors, and photocatalysts [14, 15]. CuO thin films can be obtained by various methods: electrodeposition [16], chemical vapor deposition [17], sol–gel [18], magnetron sputtering [19], spray pyrolysis [20], and thermal evaporation [21]. Among these methods, spray pyrolysis is distinguished by simple implementation, high speed of deposition of layers, and the lack of complex technological equipment. Provided that this method produces satisfactory materials for photoconverters, it can significantly reduce the cost of obtaining them.

2. Experimental details

Spray pyrolysis is one of the most common methods for the deposition of metal oxides, such as ZnO, NiO, and CuO, with low cost and high deposition surface [20, 22].

Thin films of CuO of p-type conductivity were deposited by spray pyrolysis method using 0.2 M (molar) of the aqueous solution of $CuCl_2 \cdot 2H_2O$.

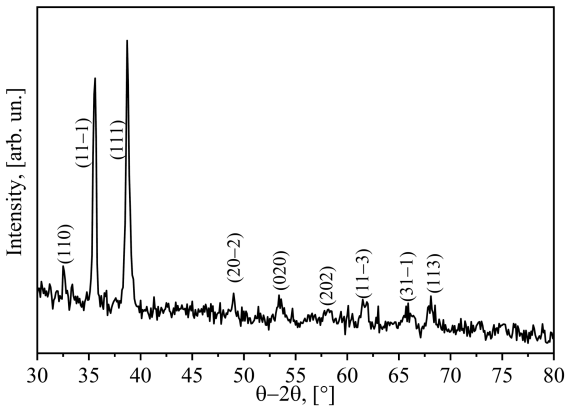

Fig. 1. XRD patterns of CuO film deposited on glass substrate.

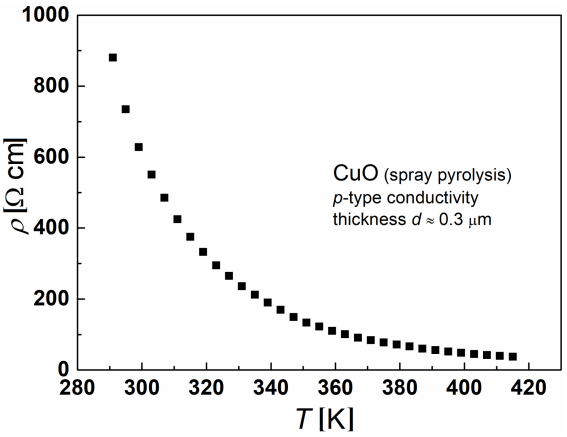

Fig. 2. Temperature dependence of resistivity $\rho = f(T)$ of CuO thin films.

The solution was sprayed in small drops onto the preheated glass and ceramic glass substrates. The pyrolysis temperature was $T_S = 350$°C. Films on the substrate surface were formed by a pyrolytic decomposition reaction.

The film crystal structure was investigated by X-ray diffraction (XRD) using a DRON-3M diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm) as the source. The scan rate of 1°/min and a step size of 0.1° were used.

Samples of films on 18×18 mm^2 glass were used to study the optical properties. Measurements of electrical parameters were carried out on samples of films on ceramic glass substrates, which were formed with specified geometric dimensions. Copper wires, which were connected with silver paste, were used to make electrical contacts.

The thickness of CuO films was measured using Interferometer MII-4. Transmission spectra in the visible region and the infrared range were studied on the SF-2000 spectrometer and Nicolet 6700 spectrometer, respectively.

3. Results and discussion

The XRD pattern of the copper oxide film is shown in Fig. 1. The sample revealed strong diffraction peaks at 35.5 and 38.7°, which correspond to the crystallographic reflections of (11-1) and (111) of planes. The sample also revealed weak maxima at 32.5°, 48.7°, 53.4°, 58.4°, 61.5°, 66.2°, and 68.0°, which are due to, respectively, (110), (20-2), (020), (202), (11-3), (31-1), and (113) planes of monoclinic CuO phase, which corresponds to the JCPDS card No. 00-048-1548. No additional reflections of other phases or impurities were found on the XRD pattern, which indicates a corresponding purity of synthesized single-phase CuO films.

The values of the full width at half maximum (FWHM) of the main peaks ($\overline{1}11$) and (111) planes were also obtained from the analysis. Based on FWHM, we can calculate the size of coherent scattering regions (CSR) of the film. The CSR were estimated for the sample using Debye–Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos(\theta)}, \tag{1}$$

where D, λ, θ, and β are the CSR, the X-ray wavelength of Cu K_{α_1} radiation, the Bragg diffraction angle, and the FWHM of the (002) diffraction peak, respectively. The grain size of the calculated CSR from the XRD analysis is 24 nm.

To achieve high efficiency of semiconductor devices, efficient removal of electrical current carriers is necessary. This function is performed by means of metal contacts, which are brought to a thin film or semiconductor structure. The main requirement for them is that they must have ohmic properties, i.e., low electrical resistance and linear volt–ampere characteristic. These conditions are met by creating a contact area (from the semiconductor) enriched by the main charge carriers. The relationship between the work function of electrons from a semiconductor and a metal is not the only factor in creating an ohmic contact. Particular attention should be paid to the surface phenomena of the substance, the degree of doping of the semiconductor material, and the possible formation of various chemical compounds or structures at the point of contact. To determine the electrical parameters of CuO thin films, we used ceramic glass with specified geometric dimensions as a substrate. Copper wires, which were connected with silver paste, were used to make electrical contacts. To measure the temperature dependence of the resistivity of thin films of copper oxide, contacts were made on two opposite sides of the film.

Figure 2 shows the temperature dependence of the resistivity $\rho = f(T)$ of CuO thin films. Measurements of temperature dependence were performed in the temperature range of 290–420 K. It can be seen in Fig. 2 that the resistivity

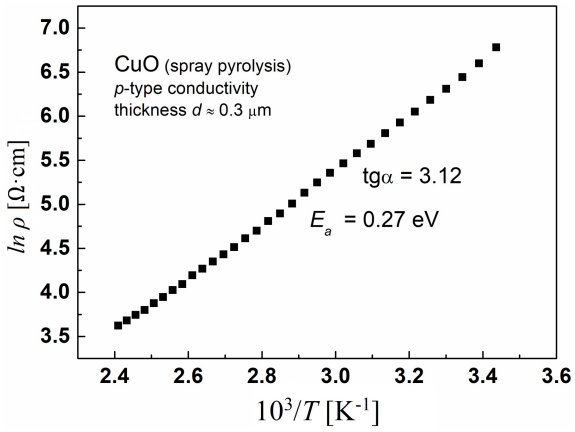

Fig. 3. Arrhenius plot $\ln(\rho) = f(10^3/T)$ of CuO thin films.

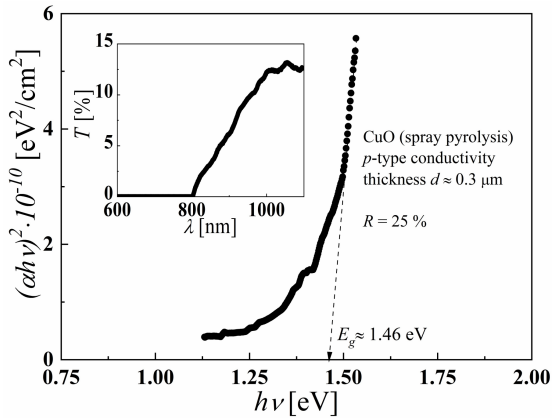

Fig. 4. Spectral dependence $(\alpha h\nu)^2 = f(h\nu)$ and $T = f(\lambda)$ (on the insert) of CuO thin films, obtained by spray pyrolysis at $T_S = 350$°C.

decreases with increasing temperature. This temperature dependence of resistivity shows that copper oxide thin films have semiconductor-type conductivity.

Figure 3 shows the Arrhenius plot $\ln(\rho) = f(10^3/T)$ of CuO thin films. The tangent of the tilt angle $\tan(\alpha) = 3.12$ and the activation energy $E_a = 0.27$ eV were determined. Values of the activation energy ($E_a = 0.27$ eV) are smaller than half of the CuO band gap. The calculated activation energies are smaller than the optical band gap energy ($\ll E_g/2$), which may indicate that the conduction is due to the transition of charge carriers from the valence band to the working acceptor level [23]. The activation energy for CuO thin films varies within the wide range of 0.08–0.57 eV obtained by the spray pyrolysis method [24], so it is very difficult to establish its nature accurately.

The transmittance T of the studied samples of CuO films of appropriate thickness d and refractive index n in the absence of interference and taking into account the relationship between n and the extinction coefficient (k) $n^2 \gg k^2$ at which the condition $\alpha\lambda/(4\pi n) < 1$ is met, is described by the formula [25]

$$T = \frac{\left(1-R\right)^2 \exp\left(-\alpha d\right)}{1-R^2 \exp\left(-2\alpha d\right)}. \tag{2}$$

The absorption coefficient can be calculated from the formula

$$\alpha = \frac{1}{d}\ln\left(\frac{\left(1-R\right)^2}{2T} + \sqrt{\frac{\left(1-R\right)^2}{4T^2} + R^2}\right). \tag{3}$$

The use of formula (3) to calculate α is due to the lack of interference pattern on the spectral dependence of the transmittance of CuO films, which made it possible to dismiss interference phenomena at the interface between the film-substrate. The reflection coefficient of the films in the studied region of the spectrum varies within $R \approx 9$–14%.

Data from optical studies were analyzed based on the formula [26]

$$\alpha = \frac{B^2\left(h\nu - E_g\right)^n}{h\nu}, \tag{4}$$

where B is a constant, and n is a constant that depends on the type of optical transition. For direct transitions, $n = \frac{1}{2}$.

Figure 4 shows the spectral dependence of the transmittance T (insert) and $(\alpha h\nu)^2 = f(h\nu)$ for CuO films. At wavelengths $\lambda > 0.95$ μm, the transmittance is $T = 9$–14%. By extrapolating the rectilinear sections to the zero value of the absorption coefficient, the values of the band gap $E_g = 1.46$ eV are obtained.

It should be noted that the optimal mode of spray pyrolysis was used to obtain thin films of CuO. They have a near-optimal band gap for photoconverters at relatively low manufacturing temperatures $T_S = 300$°C. Similar values of E_g (1.47 eV) were observed by the authors [27] at lower pyrolysis temperature $T_S = 300$°C.

4. Conclusions

Thin films of CuO of p-type conductivity were deposited by spray pyrolysis method using 0.2 M of the aqueous solution of $CuCl_2 \cdot 2H_2O$. Using XRD analysis, it was determined that the CuO thin films are single-phase with the monoclinic type of crystal structure.

Spray pyrolysis at the temperature $T_S = 350$°C using 0.2 M aqueous solution of copper dichloride $CuCl_2 \cdot 2H_2O$ produces thin films of CuO of p-type conductivity up to 300 nm thick with close to optimal for photoconverters optical value of the band gap $E_g = 1.46$ eV.

From the study of electrical properties, it was found that the resistance of CuO thin films decreases with increasing temperature, i.e., CuO has semiconductor-type conductivity.

Acknowledgments

We express many thanks to all Polish people and the Organizers of the "Jaszowiec 2022" conference for Solidarity with Ukraine in this hard time. Also, we are very grateful to the Armed Forces of Ukraine for giving us the opportunity to prepare this article.

References

[1] E.M. Alkoy, P. Kelly, *Vacuum* **79**, 221 (2005).

[2] B.D. Yao, Y.F. Chan, N. Wang, *Appl. Phys. Lett.* **81**, 757 (2002).

[3] J. Ghijsen, L.H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, *Phys. Rev. B* **38**, 11322 (1988).

[4] H. Parkhomenko, M. Solovan, V.V. Brus, E. Maystruk, P.D. Maryanchuk. *Opt. Eng.*, **57**, 017116 (2018).

[5] J. Morales, L. Sanchez, F. Martin, J.R. Ramos-Barrado, M. Sanchez, *Thin Solid Films* **474**, 133 (2005).

[6] S.H. Choi, J.P. Choi, *J. Res. Environ. Earth Sci.* **3**, 47 (2017).

[7] Z. Werner, J. Gosk, A. Twardowski, M. Barlak, C. Pochrybniak, *Nucl. Instrum. Methods Phys. Res. B* **358**, 174 (2015).

[8] M. Xu, H. Yuan, B. You, P.F. Zhou, C.J. Dong, M.Y. Duan, *J. Appl. Phys.* **115**, 093503 (2014).

[9] M. Balik, V. Bulut, I.Y. Erdogan, *Int. J. Hydrogen Energy* **44**, 18744 (2019).

[10] M. Yuan, X. Guo, H. Pang, *Mater. Today Chem.* **21**, 100519 (2021).

[11] S. Dey, G.C. Dhal, *Mater. Today Chem.* **17**, 100282 (2020).

[12] D. Prasanth, K.P. Sibin, H.C. Barshilia, *Thin Solid Films* **673**, 78 (2019).

[13] X. Yu, Y. Xuan, *Solar Energy* **160**, 200 (2018).

[14] N. Abraham, A. Rufus, C. Unni, D. Philip, *Spectrochim. Acta A: Mol. Biomol. Spectr.* **200**, 116 (2018).

[15] S. Ahmmed, A. Aktar, *Superlattices Microstruct.* **151**, 106830 (2021).

[16] Q. Ma, X. Shi, L. Bi, J. Li,Q. Zhou, B. Zhu, *Superlattices Microstruct.* **151**, 106815 (2021).

[17] J. Zhang, Z. Yang, Li Sun, *J. Mater. Sci. Mater. Electron.* **29**, 4495 (2018).

[18] F. Wang, H. Li, Z. Yuan, *RSC Adv.* **6**, 79343 (2016).

[19] S. Kuryshchuk, T. Kovalyuk, H. Parkhomenko, M. Solovan, *East Eur. J. Phys.* **4**, 76 (2021).

[20] R. Daira, A. Kabir, B. Boudjema, C. Sedrati, *Solid State Sci.* **104**, 106254 (2020).

[21] K. Sahu, S. Choudhary, S.A. Khan, A. Pandey, S. Mohapatra, *Nano-Struct. Nano-Objects* **17**, 92 (2019).

[22] H.P. Parkhomenko, M.N. Solovan, A.I. Mostovoi, I.G. Orletskii, O.A. Parfenyuk, P.D. Maryanchuk, *Opt. Spectrosc.* **122**, 944 (2017).

[23] A.D. Faisal, W.K. Khalef, *J. Mater. Sci. Mater. Electron.* **28**, 18903 (2017).

[24] P. Datta, M. Sharmin, J. Podder, S. Choudhury, *J. Optoelectron. Adv. Mater.* **23**, 35 (2021).

[25] Y.I. Ukhanov, *Optical Properties of Semiconductors* Nauka, Moscow 1977 (in Russian).

[26] I.G. Orletsky, M.I. Ilashchuk, E.V. Maistruk, H.P. Parkhomenko, P.D. Marianchuk, I.P. Koziarskyi, D.P. Koziarskyi, *Mater. Res. Express* **8**, 015905 (2021).

[27] M.L. Zeggar, F. Bourfaa, A. Adjimi, F. Boutbakh, M.S. Aida, N. Attaf, *Eng. Technol. Int. J. Phys. Math. Sci.* **9**, 632 (2015).