Conference materials
UDC 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.173.159

Optical properties of the CuO-ZnO thin films

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Abstract. In this work, we investigate the optical properties of CuO-ZnO thin films formed on quartz substrate. CuO-ZnO nanocomposite films were obtained by solid-phase pyrolysis with different atomic Cu:Zn ratios (1:99, 3:97, 5:95, 10:90) and annealed at a temperature of 600 °C. The crystal structure of the films was studied, and their optical transmission spectra were analyzed. It was found that transmittance is more than 84% for all materials in the range from 400 to 1000 nm.

Keywords: zinc oxide, copper oxide, composite, thin films, optical properties

Funding: The work was supported by Grant 4L/22-04-PISH carried out at the Southern Federal University.

Citation: Ignatieva I.O., Starnikova A.P., Petrov V.V., Bayan E. M., Optical properties of the CuO-ZnO thin films, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.1) (2024) 293–296. DOI: https://doi.org/10.18721/JPM.173.159

Материалы конференции
УДК 546.05; 538.975
DOI: https://doi.org/10.18721/JPM.173.159

Оптические свойства тонких пленок CuO-ZnO

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Аннотация. В работе изучаются кристаллическая структура и оптические свойства тонких пленок CuO-ZnO, сформированных на подложках из кварцевого стекла. Нанокомпозитные пленки CuO-ZnO получали методом твердофазного пиролиза с молярным соотношением Cu:Zn (1:99, 3:97, 5:95, 10:90). Установлено, что коэффициент пропускания составляет более 84% для материалов в диапазоне длин волн 400-1000 нм.

Ключевые слова: оксид цинка, оксид меди, тонкие пленки, оптические свойства

Финансирование: Работа выполнена при поддержке гранта 4L/22-04-ПИШ в Южном федеральном университете.

Ссылка при цитировании: Игнатьева И.О., Старникова А.П., Петров В.В., Баян Е.М. Оптические свойства тонких пленок CuO-ZnO // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.1. С. 293–296. DOI: https://doi.org/10.18721/JPM.173.159

Introduction

Nowadays, special attention is being paid to the development of multifunctional materials that can be used in various industries. One of these materials is zinc oxide, is a wide-band n-type conductor (E_g = 3.37 eV) [1]. Materials based on it are used in electronic and optoelectronic devices such as semiconductor lasers and LEDs in the ultraviolet (UV) region of the spectrum [2], solar cells [3] and gas sensors [4].

There are many physical and chemical synthesis methods, such as pulsed laser deposition [5], magnetron sputtering [6], sol-gel [7] and spray pyrolysis [8]. It is known that the creation of a p-n heterojunction has a beneficial effect on various properties of the materials obtained. Thus, the combination of ZnO with p-type semiconductors such as CuO, NiO, Co_3O_4 and Cr_2O_3 allows the use of chemical sensors, magnetic drives and optical devices [9].

The article [10] reports on the production of CuO-ZnO thin films by radio frequency sputtering. Based on the optical transmission spectra, it was found that the transmission coefficient and the band gap decrease with increasing film thickness and CuO content, which is explained by hybridization between CuO and ZnO to form a composite material.

In this paper, we report on the structural and optical properties of CuO-ZnO thin films obtained by solid-phase pyrolysis. The results showed that the obtained materials are promising candidates for creation of the optical devices.

Materials and Methods

Zinc (II) acetate dihydrate, copper (II) acetate dihydrate and organic acid $C_{20}H_{30}O_2$ were used to produce thin CuO-ZnO films by solid-phase pyrolysis. The process of forming thin films consisting of two stages conducted according to the previously described method [11, 12]. The films were annealed at 600 °C during 2 h. We have studied the phase composition of the film materials and crystalline quality by X-ray phase analysis (XRD) on an ARL'XTRA diffractometer, Cu-Kα radiation. The optical properties of obtained thin films were studied using an optical transmittance spectrum obtained on a UV-1100 spectrophotometer.

Results and Discussion

Fig. 1, *a* demonstrates X-ray diffraction patterns of CuO-ZnO thin films with different atomic Cu:Zn ratios (1:99, 3:97, 5:95, 10:90) in the 2 theta range 20–80°.

The obtained materials are polycrystalline in nature and two-phase. In addition to the peaks of the hexagonal structure of wurtzite of zinc oxide, there are peaks characteristic of tenorite CuO, having a monoclinic crystal structure. Diffractograms of the obtained materials were compared with standard sample ZnO and CuO from the database. Moreover, the intensity of the peaks of zinc oxide wurtzite is much more pronounced than the peaks of copper oxide. No other phases were found in the synthesized materials, which indicates the purity of the obtained material.

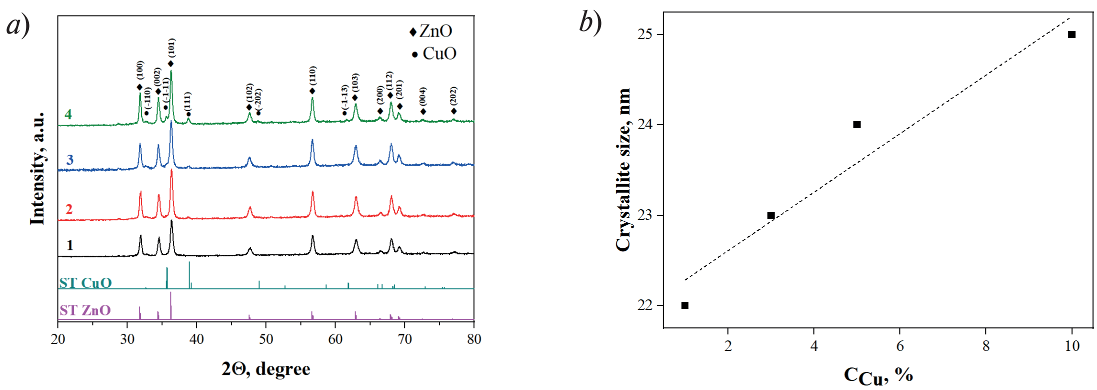

Fig. 1. X-ray images of CuO-ZnO films with Cu:Zn of 1:99 (1), 3:97 (2), 5:95 (3), 10:90 (4) and standard sample from the database (curve ST ZnO and ST CuO) (*a*) and dependences of the crystallite size on the CuO content (*b*)

The particle size was estimated with the Scherrer equation (Fig. 1, *b*). The crystal sizes range from 22–25 nm. The ZnO particle size increases with increasing CuO content in the film.

Optical transmittance spectra are shown in Fig. 2. It was determined that the obtained materials are optically transparent in the range from 400 to 1000 nm with a transmittance of more than 84%. Thin film with an atomic ratio Cu:Zn = 3:97 has the least transmittance in the visible light range, and the highest transmittance in the UV light range of 94%.

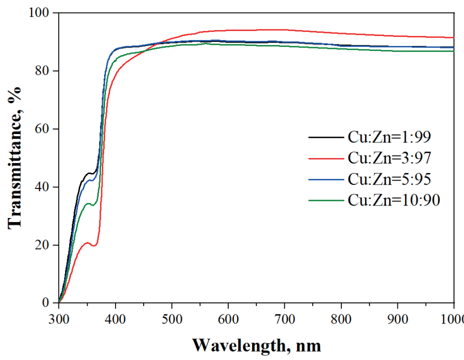

Fig. 2. Optical transmittance spectra of CuO-ZnO films of various composition

Based on the measured optical absorption spectra, Tauck graphs were obtained: $\alpha^2 = f(h\nu)$ and $\alpha^{1/2} = f(h\nu)$ and the optical absorption boundary characterizing the band gap was determined [13]. The assessment took into account the fact that indirect interband transitions can occur in complex semiconductors, which include metal oxides. Table shows the values of the band gap for direct and indirect crossings.

Table

The band gap of the CuO-ZnO thin films

Composition	$E_g(\alpha^2)$, eV	$E_{g1}(\alpha^{1/2})$, eV	$E_{g2}(\alpha^{1/2})$, eV
Cu:Zn of 1:99	4.00	3.18	3.45
Cu:Zn of 3:95	3.98	3.12	3.34
Cu:Zn of 5:97	3.98	3.14	3.40
Cu:Zn of 10:90	3.98	3.12	3.38

The value of the band gap for direct transitions $E_g(\alpha^2)$ CuO-ZnO thin films is significantly higher than that of pure ZnO obtained by solid-phase pyrolysis technology and equal to 3.30 eV. The obtained values of $E_g(\alpha^2)$ are close to the values of the band gap of Co_3O_4-ZnO films obtained in [12]. This can be explained by the fact that a large concentration of charge carriers is observed in the conduction band, leading to an observed increase in the energy of direct transitions. Two levels of indirect transitions $E_{g1}(\alpha^{1/2})$ and $E_{g2}(\alpha^{1/2})$ are also present on the Tauck graphs, the energies of which are significantly lower than the value of $E_g(\alpha^2)$. The values of $E_{g1}(\alpha^{1/2})$ correspond to the values of the band gap of $Zn_{1-x}Cu_xO$ films ($x = 0.01$ or 0.02) obtained in [14]. At the same time $E_{g2}(\alpha^{1/2})$ are close to the values of the band gap of zinc oxide ZnO [1].

Conclusion

CuO-ZnO thin films were obtained by solid-phase pyrolysis on quartz substrate. The material is two-phase, which is confirmed by the presence of peaks characteristic of ZnO and CuO. The particle size increase with increasing the copper oxide content. Transmittance is more than 84% for all materials in the range 400–1000 nm. The obtained materials can be used as optical devices.

Acknowledgments

The work was supported by Grant 4L/22-04-PISH carried out at the Southern Federal University.

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Received 11.07.2024. Approved after reviewing 31.07.2024. Accepted 01.08.2024.