

Synthesis of Nanocrystalline Composite CuO-ZnO Thin Films for Photovoltaic Sensors [†]

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Abstract: Nanocrystalline CuO-ZnO composite thin films were obtained by solid-phase pyrolysis with different molar ratios of Cu:Zn (1:99 and 5:95). X-ray diffraction analysis showed that the films are composed of two phases. According to scanning electron microscopy data, the film is solid and is formed by crystallites with an average size of 18 nm. The films have high transparency in the visible range.

Keywords: thin films; zinc oxide; copper oxide; composite; photovoltaic sensor

1. Introduction

One of the promising areas in modern chemistry is the development of multifunctional film materials with specific physical and chemical characteristics. Zinc oxide is attracting particular attention due to its properties as an n-type semiconductor with a wide band gap ($E_g = 3.37$ eV) [1]. Materials based on it are used in the production of optical devices [2], varistors [3], and solar cells [4].

The synthesis of thin films is achieved by various methods, such as pulsed laser deposition [5], sol-gel [6], radio frequency magnetron sputtering [7] and spray pyrolysis [8]. It has been established that the formation of a p-n heterojunction through the doping of zinc oxide with materials having p-type conductivity, such as, Co_3O_4 , CuO, and NiO, can lead to the creation of a photosensitive resistive materials [9,10].

Such materials also make it possible to obtain photodiodes with good performance. Thus, the paper [11] reports on the production of ZnO:Cu (n-CZO) thin films by pulsed laser deposition on silicon with p-type conductivity (p-Si). It was found that when exposed to visible light, the photoreceptor of the n-p transition (n-CZO/p-Si) in reverse bias mode has a rise time and fall time of less than 150 ms.

In this paper, we report on the production of nanocrystalline CuO-ZnO composite thin films by solid-phase pyrolysis. The presented results indicate the potential use of CuO-ZnO as a material for photosensitive elements.

2. Materials and Methods

The starting chemicals of zinc (II) acetate dihydrate, copper (II) acetate dihydrate and organic acid $\text{C}_{20}\text{H}_{30}\text{O}_2$ were used to form thin CuO-ZnO films by solid-phase pyrolysis with a molar ratio Cu:Zn = 1:99 and 5:95. The synthesis of producing thin films is consist

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of two stages and described in previous studies [12]. At the first stage, an intermediate product was obtained, which is a mixture of zinc and copper salts. Then, a solution of this intermediate product in an organic solvent was applied to pre-prepared substrates. The films were annealed at 600 °C during 2 h.

The materials were examined by X-ray phase analysis (XRD) on an ARL XTRA diffractometer, CuK α 1-radiation. Dislocation density (δ) and strain (ϵ) were calculated using the mathematical equations [13]. By scanning electron microscopy (SEM, scanning electron microscope Nova Nanolab 600) at 10 keV the surface morphology and thickness of the obtained materials were investigated. Spectra of the prepared films were measured with a UV-1100 ECOVIEW spectrophotometer in the wavelength range of 200–1100 nm at ambient temperature. The band gap (E_g) was determined using Tauc plots.

3. Results and Discussion

3.1. XRD

X-ray diffraction patterns of nanocrystalline composite CuO-ZnO thin films are presented in Figure 1. The obtained materials are polycrystalline in nature and two-phase. The main phase is the hexagonal structure of wurtzite ZnO. However, with increasing additive content, peaks of the monoclinic crystal structure of CuO appear. Thus, the XRD analysis confirm the production of the CuO-ZnO composite material. No other phases were detected.

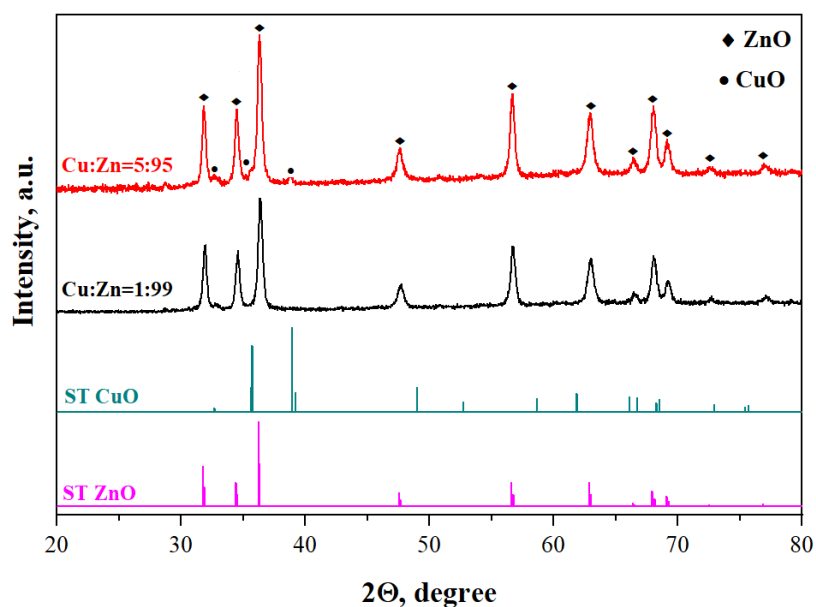


Figure 1. X-ray images of CuO-ZnO films with Cu:Zn = 1:99 and 5:95 and standard sample from the database (curve ST ZnO and ST CuO).

The intensity of the wurtzite peaks is much more pronounced than that of the tenorite peaks. Furthermore, the intensity of the peaks increases as the copper concentration increases, which can be attributed to an improvement in the degree of crystallinity of the obtained materials. The dislocation density (δ) and strain (ϵ) and are listed in Table 1. Both parameters decrease, indicating a reduction in the number of defects occurring during film formation.

Table 1. Measurement of dislocation density and strain of CuO-ZnO thin films.

Composition	$\Delta \times 10^{-3} \text{ (nm}^{-2}\text{)}$	$E \times 10^{-3}$
Cu:Zn = 1:99	2.09	5.27
Cu:Zn = 5:95	1.81	4.90

3.2. SEM

According to SEM data, the surface of the film is solid and has a uniform distribution of well-formed crystallites. The average size of the crystallites is 18 nm. The film is composed of ZnO and CuO nanocrystallites that are evenly distributed throughout the film and are in contact with one another. This arrangement leads to the formation of n-p heterojunctions between the two oxides.

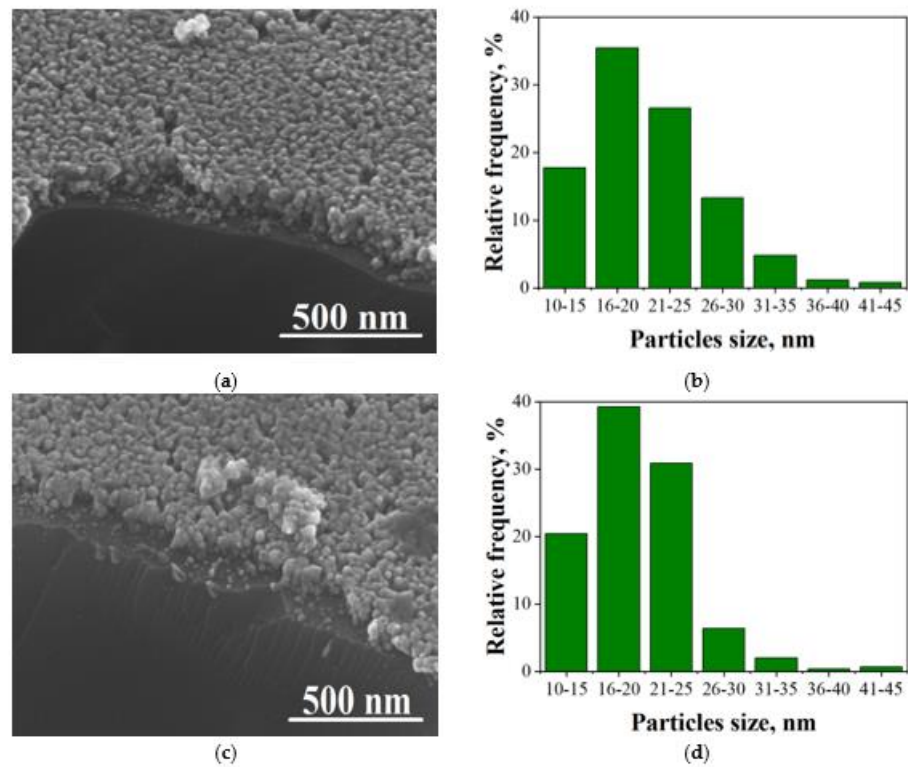


Figure 2. SEM photos of surface (a,c) b distribution of nanocrystallites (b,d) in Cu:Zn = 1:99 (a,b) and 5:95 (c,d).

3.3. Optical Properties

As can be seen from the calculations, CuO-ZnO thin films have a fairly high dislocation density, which indicates a high defect in the film structure. As a rule, films with such a structure have a complex type of optical absorption spectra, which is due to the existence of indirect interband transitions [14]. For them, the dependence of the absorption coefficient on the photon energy is more complex, which in general can be described by the function:

$$\alpha^{1/2} = f(h\nu), \text{ if } \Delta E_g - E_p < h\nu < \Delta E_g + E_p \tag{1}$$

where α is the absorption coefficient; h is Planck’s constant; ν is the frequency of optical radiation; ΔE_g is the band gap; E_p is the energy of a photon that is absorbed or emitted during indirect transitions.

Using the technique described in [15], the band gap and indirect interband transitions were determined using optical absorption spectra (Figure 3).

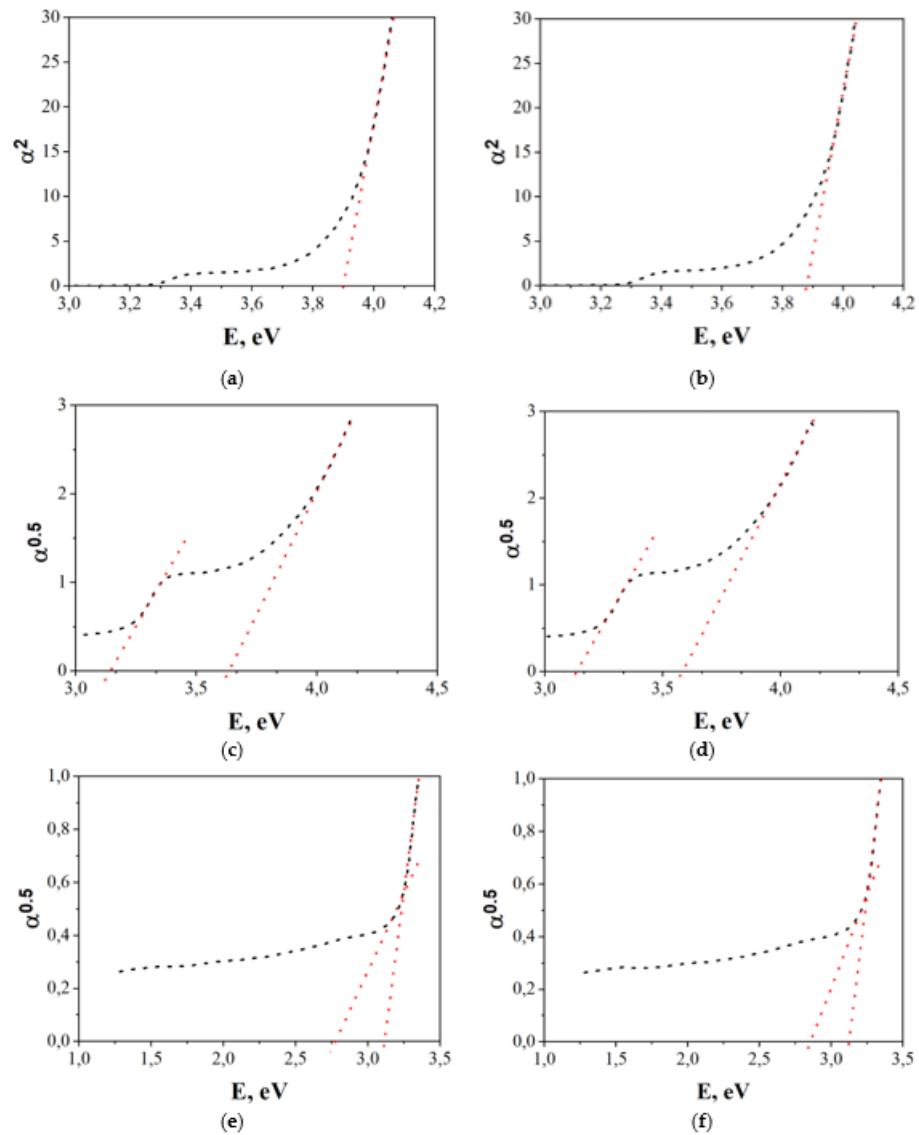


Figure 3. Determination of the band gap (a,b) and indirect interband transitions (c–f) for materials 1CuO-99ZnO (a,c,e), 5CuO-95ZnO (b,d,f).

The band gap width $E_g(\alpha^2)$ of 1CuO-99ZnO thin films is 3.90 eV, and 5CuO-95ZnO is 3.87 eV. This is significantly higher than that of pure ZnO obtained by the same technology and equal to 3.26 eV [16]. The obtained $E_g(\alpha^2)$ values are close to the band gap values of Co_3O_4 -ZnO films obtained by us in the work [10]. An increase in the energy of direct transitions can occur as a result of the occupation of possible states in the conduction band by charge carriers [14]. It is evident from Figure 3a,b that it is also possible for there to be electron transition energies that are determined by film defects. Such transitions are determined by the $E_g(\alpha^{0.5})$ dependences, which are shown in Figure 3c–f. The transition energy equal to 3.65 eV for 1CuO-99ZnO and 3.58 eV for 5CuO-95ZnO is close to the band gap of copper-doped zinc oxide ($E_g = 3.3$ – 3.5 eV) [17]. It follows from the data in Figure 4c,d that transitions with lower energy are also present in the film. A more thorough analysis of this region (Figure 3e,f) showed that the energies are 2.78 and 3.13 eV for the 1CuO-99ZnO film; the energies are 2.87 and 3.13 eV for the 1CuO-99ZnO film. The found energy values of 2.78–2.81 eV correspond to the electron jump between the donor level of Cu^{2+} and the acceptor level of Cu^+ . And the transition energy of 3.13 eV can

correspond to transitions both between the acceptor level of Cu^+ and the bottom of the conduction band, and between the vacancies of Zn and the top of the valence band [17].

Thus, the complex structure of the obtained films and the presence of copper (II) oxide crystallites actually leads to a narrowing of the forbidden band of the CuO-ZnO composite to 2.8 eV. As a consequence, the obtained materials will be sensitive not only to UV light, but also to visible radiation. This suggests that they can be used to create photosensitive sensors of the resistive type.

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