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Study of structural properties and photoconductivity of Co_3O_4–ZnO thin films

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Abstract. In this work, we study the photoconductivity parameters of Co_3O_4–ZnO thin films formed on polycortex substrates. Co_3O_4–ZnO nanocomposite films were deposited on substrates by solid-phase pyrolysis with a Co:Zn molar ratio of 10:90, 5:95, 3:97, and 1:99 and annealed at a temperature of 600 °C. The film thickness was 150–200 nm. The crystal structure of the films was studied, and the SEM images were analyzed. After application of contact metallization, the parameters of photoconductivity were measured under the action of light from an LED with a wavelength of 400 nm.

Keywords: nanomaterials, thin films, solid-state pyrolysis, photoconductivity

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Материалы конференции
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Исследование структурных свойств и фотопроводимости тонких пленок Co_3O_4–ZnO

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Аннотация. В данной работе изучаются параметры фотопроводимости тонких пленок Co_3O_4–ZnO, образованных на поликоровых подложках. Нанокомпозитные пленки Co_3O_4–ZnO наносили на подложки методом твердофазного пиролиза с молярным соотношением Co:Zn 10:90, 5:95, 3:97, 1:99 и отжигали при температуре 600°С. Толщина пленок составляла 50–100 нм. Изучена кристаллическая структура пленок и проанализированы СЭМ изображения. После нанесения контактной металлизации были измерены параметры фотопроводимости Co_3O_4–ZnO пленок при воздействии излучения светодиода с длиной волны 400 нм.

Ключевые слова: наноматериалы, тонкие пленки, твердофазный пиролиз, фотопроводимость

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Introduction

Nowadays the development of new materials promising for alternative energy sources is attracting more and more attention from researchers. The most studied multifunctional material is zinc oxide, which is a wide-band n-type conductor (E_g = 3.37 eV [1]) with chemical and thermal stability, low toxicity, and cost. Significant interest is caused by such properties as structural [2], optical [3], electrical [4], gas-sensitive [5] and photocatalytic [6]. It is noted that the execution of materials in the form of thin films with nanoscale particles is the most desirable, since it is such materials that make it possible to obtain effective devices with unique properties.

There are many physical and chemical synthesis methods The most frequently used methods, such as pulsed laser deposition [7], chemical vapor deposition [8], magnetron sputtering [9], sol-gel [10] and spray pyrolysis [11]. It has been established that the various properties of zinc oxide films are significantly affected by the additives introduced. So, doping with group III elements (Al, Ga, In) and transition metal elements (Co, Ni, Mn and Cu) it can change the optical and electrical properties of film materials. It is known that the cobalt additive is able to increase the photoreclick of ZnO in the visible spectral range, which allows such materials to become useful for converting solar energy into chemical or electrical potentials [12].

The paper [13] reports on the study of the photoconductivity of a broadband semiconductor ZnO doped with cobalt ions ($Zn_{1-x}Co_xO$). The photoconductivity of materials demonstrates a strong dependence on the cobalt content. Thus, the data show that an increase in x increases the energy of the edge of the conduction band, which increases the ionization energy of Co^{2+}/ Co^{3+}.

In this paper, we report on the structural properties and photoconductivity parameters of Co_3O_4-ZnO thin films obtained by solid-phase pyrolysis. The results showed that the materials obtained are promising candidates for alternative energy sources.

Materials and Methods

Zinc (II) acetate dihydrate $Zn(CH_3COO)_2{\cdot}2H_2O$, cobalt (II) acetate tetrahydrate $Co(CH_3COO)_2{\cdot}4H_2O$, and organic acid were used as precursors in the solid-phase pyrolysis. The process of forming thin films consisting of two stages conducted according to the previously described method [14]. During the first stage, a mixture of zinc and cobalt salts were melted in organic acid, and intermediate product was obtained. During the second stage, a solution of the produced product in a dioxane was applied to substrates previously prepared substrates. Then the resulting films were annealed at 600 °C during 2 hours.

We have studied the phase composition of the film materials and crystalline quality by X-ray phase analysis (XRD) on an ARL'XTRA diffractometer. In the future, a counter-pin V-Ni metallization was applied to the Co_3O_4-ZnO film by the method of thermal vacuum evaporation through the mask and a flat photoresistor with an initial "dark" resistance R_0 was formed.

To investigate the surface morphology and structure of the films, Co_3O_4-ZnO was carried out by scanning electron microscopy (SEM) using a microscope NovaNanoLab 600 (FEI, Holland).

Results and Discussion

Fig. 1 demonstrates X-ray diffraction patterns of thin films based on zinc oxide doped with different concentration of cobalt ions (1–10%) in the 2 theta range 20–80°. It was established that 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 Co_3O_4. Moreover, the intensity of the peaks of zinc oxide wurtzite is much more pronounced than the peaks of cobalt oxide.

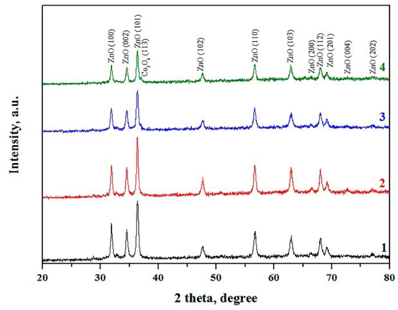

Fig. 1. X-ray images of Co_3O_4-ZnO films with a ratio of Co:Zn of 1:99 (1), 3:97 (2), 5:95 (3), 10:90 (4)

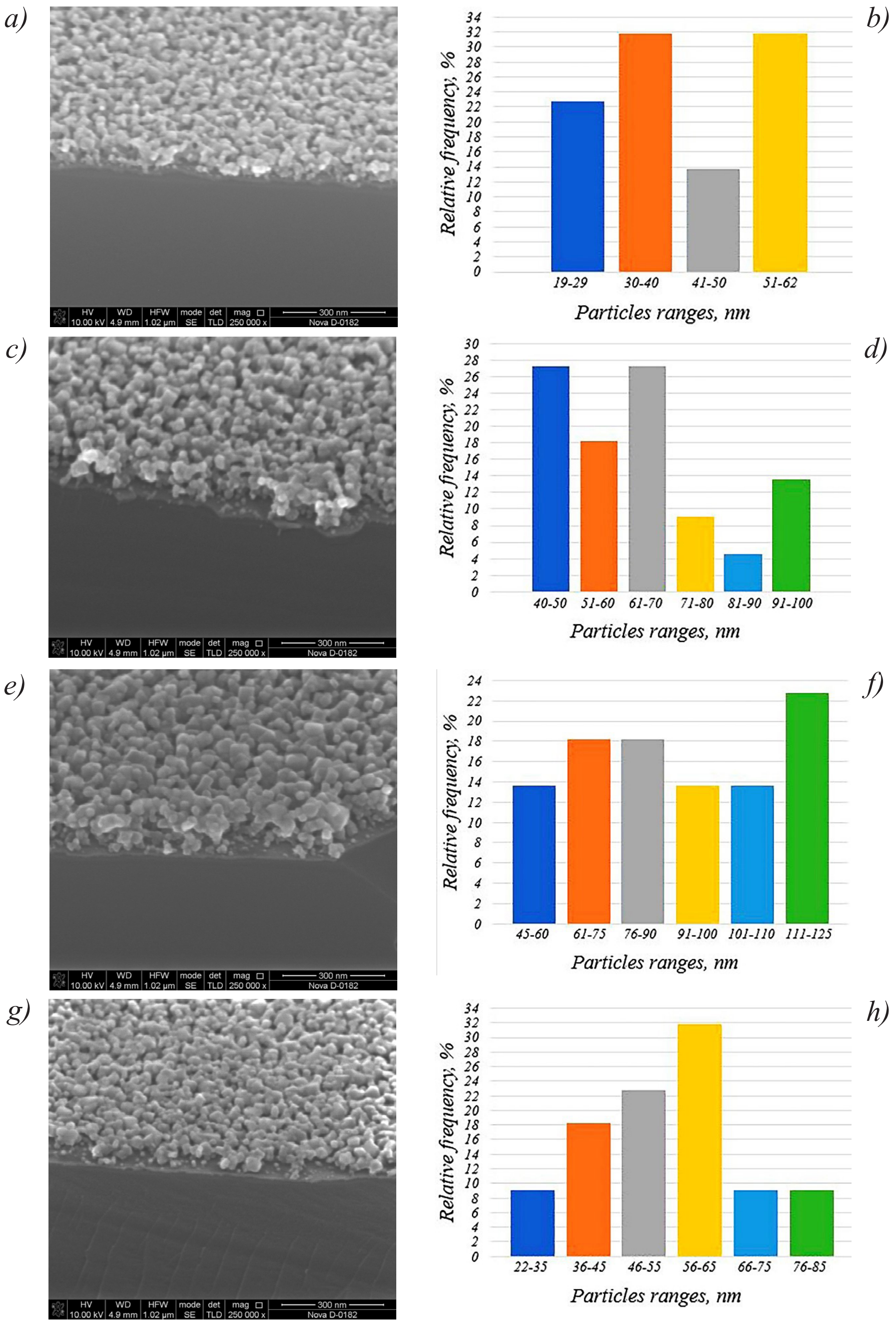

Fig.2 SEM image of Co_3O_4-ZnO films with a ratio of Co:Zn of 1:99 (*a*, *b*), 3:97 (*c*, *d*), 5:95 (*e*, *f*), 10:90 (*g*, *h*)

SEM studies showed (Fig. 2) that the thickness of the resulting films was 40–100 nm. Statistical processing of the results of EMS analysis is presented on the histograms below. It can be seen that the films have a developed relief and consist of nanoparticles, the sizes of which vary for Co_3O_4-ZnO films with a ratio of Co:Zn of 1:99 (*a*, *b*) from 19–65 nm, 40–100 nm for 3:97 (*c*, *d*), for 5:95 (*e*, *f*) it was 45–125 nm and 22-81 nm for 10:90 (*g*, *h*). Co_3O_4-ZnO films have the largest particle size with a Co:Zn of 3:97 and 5:95 ratio. Co_3O_4 particle size is reduced to 19 nm.

In order to study the parameters of the photoconductivity of thin semiconductor films and heterostructures formed on opaque substrates, a stand was designed and manufactured. The work of the stand is based on measuring the kinetics of the photoconductivity of a resistive structure based on the film under study when it is irradiated with a LED with a given wavelength. Eight LEDs with a maximum radiation wavelength of 940, 660, 625, 525, 470 and 400 nm were chosen for the research. In addition, the design of the stand includes a pulsed constant voltage power supply AKIP-1101 (Russia), which makes it possible to regulate the energy characteristics of the radiation. To measure the characteristics of radiation, an ultraviolet radiation intensity meter CENTER 532 (China) and an illumination meter (luxmeter) CENTER 530 (China) are used. The electrical contact is provided by tungsten probes, and the photoconductivity is monitored with a Tektronix DMM 4050 digital multimeter (China). There was a direct change in photoconductivity under the action of light from an LED with a peak wavelength of 400 nm.

When the LED was turned on, a photoresistance was observed in all film samples. The measurement was carried out before the beginning of the “unfolding” of the dependencies. Subsequently, the time constant for the generation of charge carriers under the action of light was calculated.

Fig. 3 shows a timeline of the time change in normalized photoresistance under the action of light for films with a molar ratio of Co:Zn of 10:90, 5:95, 3:97, 1:99.

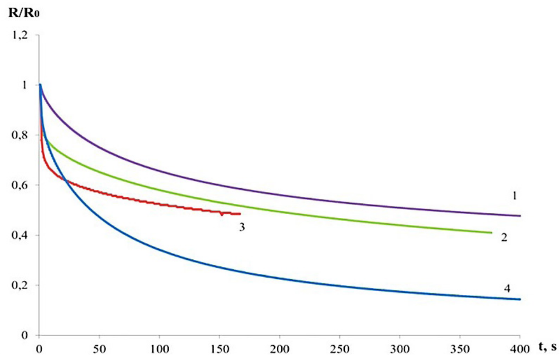

Fig. 3. Graph of the temporal change in normalized photoresistance under the action of light for Co_3O_4-ZnO films with a molar ratio Co:Zn of 1:99 (1), 3:97 (2), 5:95 (3), 10:90 (4)

Studies have shown that a film with an additive of 1% cobalt has the longest constant time equal to 70 s. Adding cobalt oxide of 3% and 10% drastically reduces the constant duration to 37 and 60 s. The fastest response time of 25 s was found in a sample with a Co:Zn ratio of 5:95. This behavior of photoconductivity parameters is associated with the nanocomposite structure of the film material, and lower values of the constant time are associated with a higher concentration of charge carrier generation centers at the Co_3O_4-ZnO interface at a Co:Zn ratio of 5:95. It can also be noted that the response kinetics for all films were similar, which indicates the same generation mechanisms - recombination of charge carriers in ZnO sol-gel films with the addition of CoO.

Conclusion

Based on the X-ray diffraction results, it was found that the resulting material is two-phase, which is confirmed by the presence of peaks characteristic of ZnO and Co_3O_4. It is noted that the intensity of the wurtzite peaks of zinc oxide is much more pronounced than the peaks of cobalt oxide.Thus, in this work, thin films of Co_3O_4-ZnO were synthesized by a new method of solid-phase pyrolysis, in which the phase composition and the measured kinetics of photoconductivity were investigated. that the Co_3O_4-ZnO film with a Co:Zn ratio of 5:95 has the lowest value of the time constant (25 s). At the same time, this film has the largest particle size, which may be a consequence of its speed.

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