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Structural and optical properties of Mg-doped ZnO films obtained by spray pyrolysis

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Abstract

Purpose: The paper aims to determine the optimal technological conditions for preparing metal oxide films by spray pyrolysis, as well as to study their structural and optical parameters. Zinc oxide thin films have an important combination of properties for practical application including transparency in the visible range of electromagnetic radiation and low electrical resistance which is provided by a large value of the bandgap width and by obtaining non-stoichiometric compositions or by introducing appropriate alloying elements. The possibility of practical application of ZnO thin films also depends on their optical and electrical properties.

Methods: Thin films of unalloyed zinc oxide as well as ZnO films doped with magnesium with different percentages from 1 to 15 at. % were prepared by spray pyrolysis. Structural and optical properties of magnesium-doped zinc oxide thin films were studied. Through X-ray diffraction analysis it was found that all films are polycrystalline with hexagonal wurtzite structure and crystallographic orientation (002) aligned or oriented along the plane of the substrate.

Conclusions: Studies of optical properties by UV-visible spectrophotometry showed that transmittance of magnesium-doped zinc oxide thin films increased from 70 to about 85 %, and the bandgap width increased from 3.20 to 3.42 eV. These properties of magnesium-doped ZnO thin films demonstrate their high potential for efficient use in many optoelectronic devices and instruments such as solar cells, gas sensors, allow their use as photocatalysts, etc.

Keywords: ZnO thin films, Mg doping, Spray pyrolysis method, Structural properties, Optical properties

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1. Introduction

Recently, there has been growing interest in metal oxides since thin film coatings of metal oxides are a group of the most demanded materials in modern micro- and nanoelectronics. Among them, zinc oxide (ZnO) is one of the most high-potential materials used for application of transparent electrically conductive contacts, gas sensors and piezoelectric transducers production.

ZnO is one of the most important semiconductor materials. Due to alternate placement of zinc and oxygen in the unit cell of the crystal lattice, it has the structure of wurtzite belonging to hexagonal crystal lattice and space group $P6_3mc$. Application of ZnO thin films in optoelectronic devices such as solar cells is possible due to high binding energy of excitons (60 meV) [1,2,3]. Zinc oxide ZnO with its good optoelectronic properties is often used as a transparent conducting oxide (TPO) electrode in photovoltaic devices and in planar displays. PPOs are materials that have high visible light transparency (> 80 %) and low resistivity (< 10^{-3} Ohm cm) [4,5].

Morphological, structural, optical, electrical and photodetection properties of ZnO have been studied well enough, yet influence of doping with various impurities is still insufficiently investigated. The parameters of undoped ZnO thin films are often unstable due to changes in surface conductivity by chemisorption and oxygen adsorption. Doping is an effective way to influence the surface states, electrical conductivity, formation of energy levels and concentration of charge carriers in a semiconductor. One of the important characteristics is the possibility of changing the bandgap width of ZnO by doping it with group II elements such as Be, Mg, Ca, Co, Cd and Sr. Studies of doped ZnO have shown that their properties often depend on the method of synthesis. Magnesium doped zinc oxide (MZO) thin films can be synthesized by high frequency sputtering, molecular beam epitaxy, sol-gel method, pulsed laser deposition and chemical vapor deposition [6]. In the course of the present research, the spray pyrolysis method was used since it is not labor-intensive and allows to obtain the materials with required properties through a minimum number of technological operations.

Spray pyrolysis is a method of spraying an aerosol onto a heated substrate. The aerosol is produced from a pressurized solution of metal salts which vaporizes and, once on the substrate surface, chemically reacts to form the desired properties of the substance. The possibility of moving the nozzle of the atomizer over the substrate provides homogeneous thickness of coatings on the entire surface. The main disadvantages of this method include relatively high temperatures (400 °C for ZnO) impossible to use with flexible polymer substrates [7,8].

The aim of present research is to determine the optimal technological conditions including temperature, pressure, and time for preparation of Mg-doped ZnO films with predetermined properties by spray pyrolysis, as well as to study the structural and optical parameters of the obtained MZO films.

2. Methods

To obtain the specimens by spray pyrolysis, zinc acetate dihydrate ($Zn(CH_3COO)_2$-$2H_20$) was used as the base material, and methanol and diethanolamine (DEA) were used as solvents and stabilizers. First, 5 g of zinc acetate dihydrate was dissolved in 30 mL of methanol, and then diethanolamine was added slowly using a magnetic stirrer to obtain a solution with a molar concentration of 0.75 M. ZnO doping with magnesium was carried out by adding magnesium acetate tetrahydrate $Mg(CH_3COO)_2$-$4H_2O$ along with zinc acetate to methanol. The ZnO:Mg ratio was 1 at. % for MZO specimen, 1.3 at. % for MZO specimen, 3.5 at. % for MZO specimen, 5.7 at. % for the MZO7 specimen and 15 at. % for the MZO15 specimen. 0.047 g of magnesium acetate tetrahydrate was added to the resulting solution for doping 1 at. % Mg, 0.141 g for doping 3 at. % Mg, 0.234 g for doping 5 at. % Mg, 0.328 g for doping 7 at. % Mg, and 0.705 g for doping 15 at. % Mg. The resulting mixture was stirred for 1 hour at 65 °C, and then for 3 hours at room temperature until a clear and homogeneous solution was obtained. $Zn_xMg_{1-x}O$ films were deposited by spray pyrolysis on glass substrates aged at 400°C. The distance between the atomizer and the substrate was 20 cm. The MZO films were sputtered onto the surface of preheated glass at a rate of 2.0 mL/min at an air pressure of 2 bar. Multilayer sputtering of the ZnO film was carried out for 1 min each followed by a break of 30 seconds to

restore the substrate temperature. Thus 20 layers were prepared.

Thickness of the films prepared was determined on an interference microscope MII4. Structural studies of thin films of metal oxides MZO were carried out by X-ray diffraction method on XRD-6100 diffractometer. The X-ray voltage was 40 kV and the current was 30 mA. The scanning range was 8.0-70.0 degrees, the scanning speed was 2 deg/min, and the scanning step was 0.02 degrees. Optical transmission spectra of the investigated films in the range from 200 to 800 nm were obtained on a SPEX SPP-715 M spectrophotometer.

3. Results and discussion

Thickness of the films obtained is 344.3 nm for ZnO, and it varies for different doped films. It is 348.4 nm for MZO1, 353.1 nm for MZO3, 357.6 nm for MZO5, 362.2 nm for MZO7, and 380 nm for MZO15. Thus, thickness of the films ranges from 344 to 380 nm.

X-ray diffraction patterns of ZnO:Mg thin film with Mg concentration of 1 at. %; 3 at. %; 5 at. %; 7 at. %; 15 at. % are given in Fig.1. The studies showed that all the diffraction maxima of the X-ray diffraction pattern of ZnO film belong to wurtzite structure. As Fig. 1 shows, the intensity of structural line (002) is much stronger than other diffraction lines. This indicates that thin films have a polycrystalline structure with a predominant *c* index. Fig. 2 shows that structural reflex of the crystallographic direction (002) is shifted toward small angles (from $2\theta = 34.56°$ to $2\theta = 34.44°$), i.e., toward $\Delta\theta = 0.12°$ with increasing number of doping Mg atoms in the X-ray diffraction pattern. It was found that the lattice parameters of the magnesium-doped films at room temperature are $a = b = 0.3265$ nm and $c = 0.5219$ nm, the c parameter increases insignificantly ($\Delta c = 0.0009$ nm). This, in turn, indicates that Mg^{+2} ions are substituted with Zn^{+2} in the crystal lattice of the film. In addition, we determined the half-widths (FWHM) of these reflections which first increased (doping with Mg atoms up to 7 at. %) and then decreased (doping with Mg atoms more than 7 at. %).

The obtained results indicate that the ZnO structure does not change upon addition of Mg. Sizes of the formed crystallites (D) in ZnO:Mg thin films were calculated according to Scherrer's formula [9]:

$$D = \frac{k\lambda}{\beta\cos\theta}, \quad (1)$$

where, λ is radiation wavelength of 0.154 nm, θ is scattering angle (half of the diffraction angle 2θ), β is physical line broadening on the diffractogram (width of the reflex at the half of intensity maximum), coefficient $k \approx 0.91$.

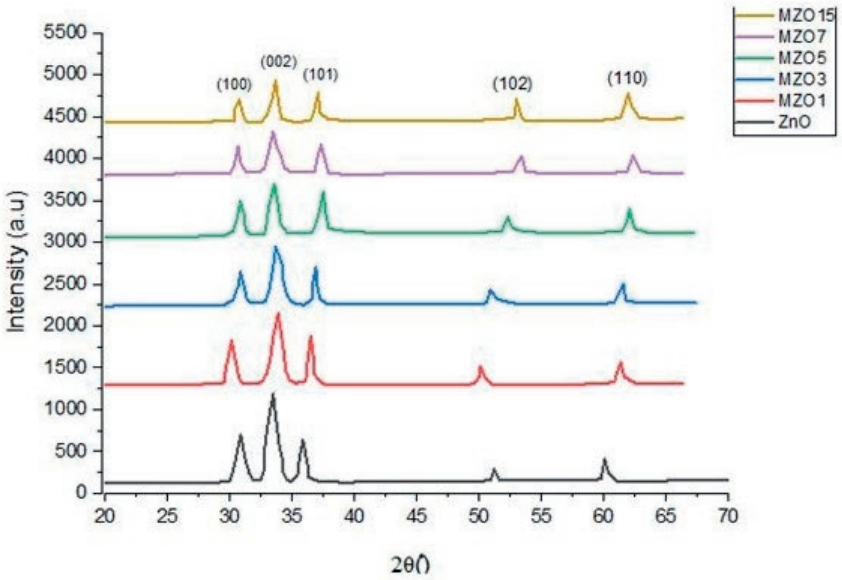

Fig. 1. X-ray images of ZnO and ZnO:Mg thin films with Mg content 1 at. %; 3 at. %; 5 at. %; 7 at. % and 15 at. %

The lattice strain ε of Mg-doped ZnO thin films can be estimated through the following expression:

$$\varepsilon = \frac{\beta \cos\theta}{4}. \quad (2)$$

The dislocation density δ is calculated as follows:

$$\delta = \frac{1}{D^2}. \quad (3)$$

The estimated values of characteristics of MZO films from the X-ray diffraction data are presented in Table 1. The results showed that with the increasing content of doping impurity Mg in MZO films from 1 to 7 at. %, the full width at half of the maximum value of peaks on X-ray diffraction decreases, i.e. the size of crystallites in the film decreases. This is probably due to the increase in the film deposition rate with increasing Mg doping degree. Consequently, the crystallite size can be controlled by varying the Mg concentration. In fact, higher doping impurity level creates more nucleation centers along with lattice defects and thus leads to a decrease in crystallite size in thin films. The results also showed that the dislocation density increases with increased Mg doping which contributes to an increase in lattice defects along grain boundaries in MZO thin films.

It is known that the peak (002) is related to film deformation. As Figs. 1, 2 show, when Mg is doped at concentrations of 1 at. %, 3 at. %, 5 at. % and 7 at. %, the diffraction peak (002) is at 2θ: 34.54, 34.50, 34.46 and 34.44 degrees, respectively. Hence, as the concentration of Mg doping impurity increases, the peak (002) gradually shifts towards a higher angle, indicating the increasing strain in the films. Magnesium doping also affects the intensity of the diffraction peak (002). An increase in the degree of doping leads to a decrease in the intensity of peak (002) compared to the similar peak in the unalloyed ZnO film (see Figs. 1, 2).

Fig. 3 shows the optical transmittance spectra of MZO films at different Mg concentrations. Obviously, with increasing Mg^{2+} concentration, the optical transmittance in the visible range increased. ZnO films doped with Mg atoms (from 1 to 15 at. %) have high transmittance from 70 to 85 % in the visible and near-infrared radiation regions. It can be seen that the ZnO film has high transmittance starting from wavelength of 387 nm. The doped MZO film (15 at. % Mg) has a high transmittance of 85 % starting from a wavelength of ~ 358 nm. When doped with Mg, transparency of the MZO film increased by 15 % compared to the undoped ZnO film, and reached its highest value at 15 at. % Mg addition. The transmission spectra of MZO thin films have a

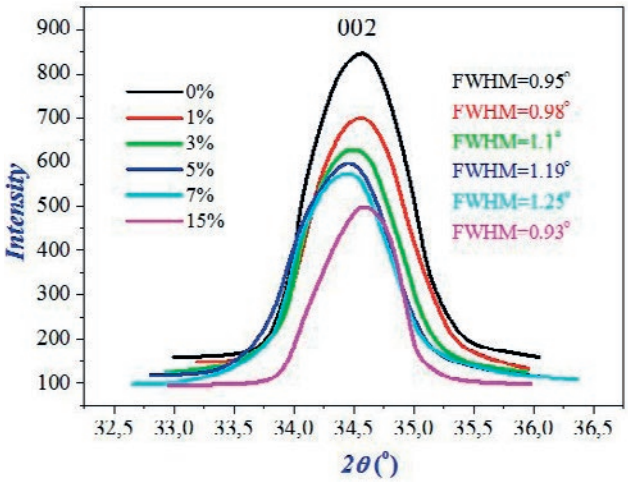

Fig. 2. Shape of reflections (002) of X-ray diffraction patterns of undoped and Mg-doped (from 1 to 15 at. %) ZnO films

Table 1. Characteristics of ZnO:Mg films obtained on the basis of X-ray diffraction data

Sample	Peak position (002) (2θ), degree	Crystallite size *D*, nm	Lattice deformation ε, degree	Dislocation density δ, nm^{-1}
MZO	34.56	92.9	$-1.15 \cdot 10^{-3}$	$1.16 \cdot 10^{-4}$
MZO1	34.54	87.6	$-1.72 \cdot 10^{-3}$	$1.30 \cdot 10^{-4}$
MZO3	34.50	78.5	$-2.7 \cdot 10^{-3}$	$1.62 \cdot 10^{-4}$
MZO5	34.46	73.05	$-3.46 \cdot 10^{-3}$	$1.87 \cdot 10^{-4}$
MZO7	34.44	69.07	$-4.19 \cdot 10^{-3}$	$2.09 \cdot 10^{-4}$
MZO15	34.59	93.02	$-1.154 \cdot 10^{-3}$	$1.15 \cdot 10^{-4}$

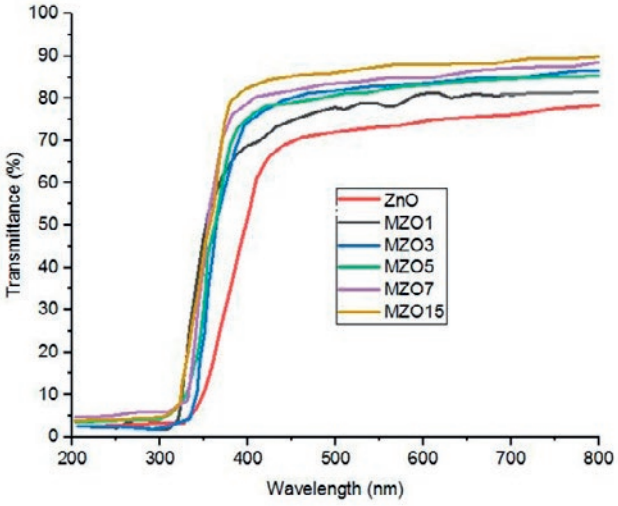

Fig. 3. Optical transmission spectra of pure ZnO films and ZnO films with different Mg dopant content

transparency of more than 80 % in the visible and infrared spectral regions. The transparency limit is in the ultraviolet range [10]. The effect of Mg doping on the bandgap width of MZO thin films was studied by the absorption spectra shown in Fig. 4. The bandgap width of unalloyed ZnO thin films and Mg-doped ZnO films was determined by the Tautz method [11] whose value can be estimated through the following expression:

$$\alpha h\nu = B(h\nu - E_g)^2, \quad (4)$$

where α is the absorption factor, $h\nu$ is the photon energy calculated on the basis of experimental results of optical transmittance (B); E_g is the forbidden band width. The absorption factor (α) can also be calculated through the following expression from transmittance (B):

$$\alpha = \frac{1}{d}\ln\frac{1}{B}, \quad (5)$$

where d is the layer thickness.

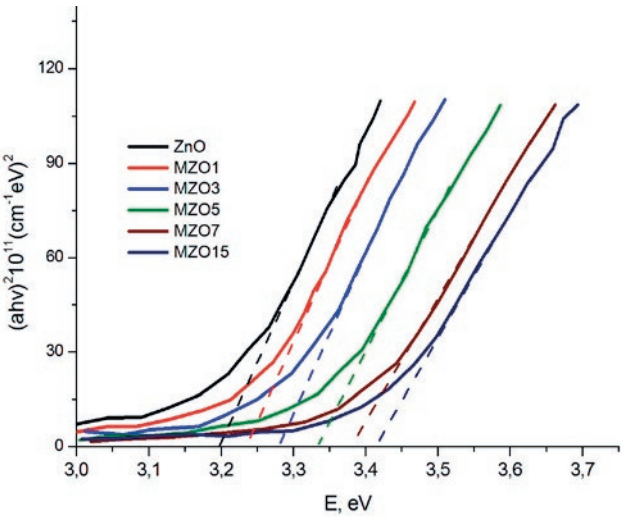

Fig. 4. Optical absorption spectra of pure ZnO films and ZnO films with different Mg dopant content

The forbidden band width of ZnO film was 3.20 eV which is the same as in ZnO films prepared by other authors [12]. Fig. 4 shows that after Mg doping, the bandgap width of ZnO gradually increased from 3.20 eV (unalloyed ZnO film) to 3.42 eV (MZO15 film with Mg content of 15 at. %). It is due to defects probably arising as a result of replacement of Mg^{2+} ions by Zn^{2+} ions in the crystal lattice of MZO film. It is known that the value of Mg^{2+} ion radius (0.57 Å) is close to that of Zn^{2+} ion radius (0.60 Å); therefore, when doping ZnO films with magnesium, inclusion of Mg^{2+} ion in the ZnO lattice is likely [13]. According to the Poling scale, their electronegativities are 1.65 for Zn and 1.31 for Mg. Due to difference in electronegativities of Zn and Mg atoms and ionic radius, formation of new point defects in the structure can cause an increase in the width of the forbidden zone. In addition, the difference in electronegativities of Zn and Mg atoms increases the width of the forbidden zone due to interaction of Mg^{2+} and O^{2-} ions. It should also be noted that the compound MgO (Eg = 7.8 eV) has a larger bandgap width than ZnO (Eg = 3.20 eV) [14].

4. Conclusions

In the course of the present research, ZnO thin films doped with Mg in various concentrations from 1 to 15 at. % were prepared by spray pyrolysis. Based on the analysis of X-ray diffraction patterns, an obvious growth of MZO films along the plane (002) with hexagonal wurtzite structure was established. With increased Mg concentration, light transmittance of MZO films increases from 70% to 85% in the visible region of the spectrum. The forbidden band width of MZO films increased with increased Mg content in the ZnO structure from 3.20 to 3.42 eV.

Properties of magnesium-doped ZnO thin films prepared can be used in many optoelectronic devices such as solar cells, gas sensors, as photocatalysts, etc.

Contribution of the authors

E. S. Rembeza responsible for scientific guidance, discussion of final conclusions, scientific editing of the paper. S. Z. Zaynobidinov responsible for scientific guidance, research concept, methodology, discussion of final conclusions. M. B. Rasulova responsible for conducting the research, discussion of final conclusions, writing the review and the text of the paper.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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