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Effect of Dopant Concentration and Crystalline Structure on Absorption Edge of ZnO:B Films

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The crystalline structure and absorption spectra of thin ZnO films with different levels of B doping are studied. The films are deposited on the glass substrates using the radio-frequency magnetron sputtering without targetedsubstrates' heating. The concentration of free charge carriers is estimated. The observed 'blue' shift of the fundamental absorption edge in the ZnO:B films with increasing of doping level is explained by the Burstein–Moss effect.

Вивчено кристалічну структуру та спектри вбирання плівок оксиду Цинку різних рівнів леґування Бором. Плівки наносили на скляні підкладинки, які цілеспрямовано не нагрівали, за допомогою високочастотного магнетронного розпорошення. Оцінено концентрацію вільних носіїв заряду та показано, що «блакитне» зміщення краю смуги фундаментального вбирання у плівках ZnO:В, яке спостерігалося зі зростанням рівня леґування, пояснюється ефектом Бурштейна-Мосса.

Key words: boron-doped zinc oxide, crystalline structure, absorption edge, optical bandgap, Burstein-Moss effect.

Ключові слова: леґований Бором оксид Цинку, кристалічна структура, край смуги вбирання, оптична заборонена зона, ефект Бурштейна–Мосса.

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1. INTRODUCTION

The semiconductor materials based on ZnO are considered as the

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best alternative to indium tin oxide, since they are much cheaper and non-toxic [1-3]. For example, ZnO:Al films possess the transmittance coefficient of approximately 90% in a visible region and are almost not inferior to ITO films by the value of resistivity $(\cong 10^{-6} \ \Omega \cdot m)$ [1]. The numerous companies around the world are involved into production of the transparent electrically conductive ZnO-based oxides for the needs of electronics (for example, 'TEL Solar' or 'NEXTECK'). The transparent conductive ZnO-based oxides are usually obtained by doping with group-III elements such as In, Al, Ga and Y [1-3]. On the other hand, the number of publications devoted to study of the properties of boron-doped zinc oxide films is not very large [4-18]. For the optimal application of ZnO:B films, it is necessary to have in-depth knowledge and understanding of their structure, optical and electrical properties. Unfortunately, one can hardly find any literature data concerning the optical properties of ZnO films with different levels of boron doping obtained with a standard radio-frequency (RF) magnetron sputtering technique.

The radio-frequency magnetron sputtering method has been widely used for fabrication of oxide thin films because of its advantages consisting in the relatively high deposition rates, low cost, easy control, and high efficiency for growing of thin films of a good quality [19].

There are a number of heat-sensitive electronic devices with the optically transparent electrodes. Therefore, at the stage of their production, the temperature should not exceed $100^{\circ}C$ [5, 6, 20].

In this paper, we report the data concerning the influence of surface morphology on the optical spectra and electrical properties of thin zinc-oxide films: pure and doped with boron in two different concentrations. The films were obtained using the RF magnetron sputtering method.

2. EXPERIMENT

The films of ZnO:B (with 0, 1 and 2 wt.% of B) were deposited by the RF magnetron sputtering on the glass substrates in argon atmosphere without substrate heating. The working gas pressure was equal to 0.1 Pa. The other important parameters were as follows: the high-frequency oscillator power of 100 W, the distance between the target and the substrate of 60 mm, the magnetic-field induction of 0.1 T. The target was prepared from a compressed mixture of ZnO (chemically pure grade) and B_2O_3 (extra pure grade) powders used in the appropriate proportions. The sputtering time was 1 hour. According to the ellipsometry data, the thickness of the films was about 0.6 µm. The surface morphology of the samples was studied using a Solver P47-PRO atomic force microscope (AFM).

The x-ray diffraction (XRD) measurements were carried out using a STOE STADI P diffractometer with a linear position-sensitive detector in a transmission Bragg–Brentano geometry ($CuK_{\alpha 1}$ radiation at $\lambda = 0.15406$ nm, Ge (111) monochromator, detector scanning step of 0.480° 20, accumulation time of 320 s, 20 angle resolution of 0.015°, 20 range—23–115 deg.).

Ex situ ellipsometry measurements were performed with a serial null-ellipsometer LEF-3 M in a standard PCSA arrangement (polar-izer-compensator-sample-analyser). He-Ne laser ($\lambda = 632.8$ nm) was used as a light source.

The absorption spectra of the films in the ultraviolet and visible regions were investigated using a portable fibre optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Apeldoorn, Netherlands) with an input slit of 25 μ m, diffraction grating of 300 lines/mm and resolution of 1.2 nm. A balanced, compact deuterium-halogen light source Avantes AvaLight-DHc (200-2500 nm) was used. Light detection in the spectrometer was carried out by a 2048 pixel CCD detector.

3. RESULT AND DISCUSSION

X-ray diffraction pattern for thin ZnO:B films (with 0.1 and 2 wt.% of B) are shown in Fig. 1. All peaks in XRD pattern were indexed to the hexagonal structure with a space group P63mc (JCPDS card No 36-1451) [3]. No additional peaks due to segregated boronrich phases have been found in any of the films under test [4, 21].



Fig. 1. X-ray diffraction pattern of as grown ZnO:B films (0, 1 and 2 wt.% of B) and the standard XRD pattern of ZnO (JCPDS card No. 36-1451).

This indicates that B ions are uniformly distributed into either Zn sites or interstitial sites in the ZnO lattice [13, 16]. Zn^{2+} and B^{3+} ions possess the radii equal to 0.074 nm and 0.027 nm, respectively, and different oxidation states [7, 8]. This causes appearance of the defects such as stress and dislocation in the thin films [16, 17]. The interplanar spacing decreases due to the smaller ionic size of boron [17]. A decrease in the intensity of (100), (002) and (101) reflection peaks with the doping concentration increasing was revealed, that testifies to a loss of crystallinity [15–18].

The average crystallite size D of undoped and B-doped ZnO films was calculated using the full width at the half maximum (*FWHM*) of the (002) and (100) diffraction peaks and the angle of diffraction θ using the Debye–Scherrer's formula [3, 13]:

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

where λ is the x-ray wavelength, β —the *FWHM*, and θ —the Bragg angle of the diffraction peak. The dislocation density δ and microstrain ε in the deposited films were calculated using the following equations [3]:

$$\delta = 1 / D^2, \qquad (2)$$

$$\varepsilon = \beta / (4 \tan \theta). \tag{3}$$

Table 1 presents the structural parameters of ZnO:B samples calculated from the XRD data.

The surface morphology of undoped and B-doped ZnO films was monitored by AFM. The dependence of crystallinity and crystallite sizes on the boron concentration was revealed by their micrographs (Fig. 2). The root mean square (RMS) roughness and average grain size were measured on 2 μ m×2 μ m area. Table 2 presents these parameters as a function of doping level.

Both the AFM and x-ray diffraction data revealed the tendency to reducing of the average size of crystallites with increasing of boron concentration.

The spectral dependence of absorption coefficient α in vicinity of the absorption edge was calculated by Bouguer-Lambert-Beer formula on the basis of the transmission spectrum. In general, the absorption coefficient is connected with the bandgap width E_g by the relation [2, 3]:

$$\alpha h \nu = B \left(h \nu - E_g \right)^r, \qquad (4)$$

where r = 1/2 for the direct allowed transitions, B is a constant,

Dopant concentration,	FWHM, deg.		Crystallite size, nm		${f Dislocation}\ { m density, 10^{16}m^{-2}}$		$\begin{array}{c} \text{Microstrain,} \\ \times 10^{-3} \end{array}$	
wt.% B	(100)	(002)	(100)	(002)	(100)	(002)	(100)	(002)
0	0.43	0.7	21.8	13.7	0.2	0.5	3	4.4
1	1.23	1.42	7.6	6.8	1.7	2.2	8.6	9
2	1.5	1.8	6.2	5.4	2.6	3.4	10.5	11.4

TABLE 1. The structural parameters of ZnO:B samples calculated on the basis of the XRD data.

TABLE 2. The RMS roughness and average grain size of ZnO:B thin films as a function of the boron concentration.

Dopant concentration, wt.% B $$	RMS roughness, nm	Average grain size, nm
0	6.4	18.6
1	4.1	18.4
2	0.4	2.2

which is practically independent on the photon energy.

The values of the optical bandgap width were obtained from the dependences of $(\alpha hv)^2$ on hv in the high absorption region using extrapolation of the linear sections of the curves to $(\alpha hv)^2 = 0$ [2, 3]. The analysis of the fundamental absorption edge using the relation (4) shows that the optical bandgap width of undoped ZnO is $E_g = 3.24$ eV (Fig. 3).

Figure 4 shows the intrinsic absorption spectra in $(\alpha h\nu)^2 = f(h\nu)$ coordinates for ZnO:B. Using the relation (4), there were obtained the corresponding values of the optical bandgap width for ZnO:B (1 and 2 wt.%) films: $E_g \approx 3.28$ and 3.38 eV.

According to the conclusions [4, 7, 10, 12, 22], the increase in the optical bandgap observed for our films due to doping with boron can be explained by a so-called Burstein-Moss effect.

According to the Burstein-Moss effect, expansion of the bandgap in an n-type semiconductor with a parabolic dispersion law for the energy bands due to doping is described by the relation [3]:

$$\Delta E_{g} = h^{2} \left(3\pi^{2} n \right)^{2/3} / \left(8\pi^{2} m^{*} \right), \qquad (5)$$

where m^* is the effective mass of the electron in the conduction band, h is Planck's constant, n is the carrier concentration. According to this formula, the bandgap width increases with increasing of the carrier concentration.

Based on relation (5), the concentration of the free charge carriers in ZnO:B films was estimated using the two known values of the



Fig. 2. AFM micrographs of the surface of ZnO films with different boron concentration: (a) undoped ZnO; (b) ZnO:B (1 wt. % B); (c) ZnO:B (2 wt. % B).

effective electron mass for ZnO $m^* = 0.24m_e$ and $m^* = 0.35m_e$ [3]. The calculations are given in Table 3.

4. CONCLUSIONS

In summary, the films of ZnO and ZnO:B (1 and 2 wt.% of B) were obtained by RF magnetron sputtering on the glass substrates without targeted heating. According to the ellipsometry measurements data, the thickness of the films was about 0.6 μ m. The crystalline structure and the absorption spectra of these films were investigated. No diffraction peaks, which would be associated with the presence of boron or its oxides in any of the investigated film, were found. The average crystallite sizes, the dislocation density and the microstrains in the films have been calculated from the x-ray dif-



Fig. 3. Absorption spectrum of 0.6 μ m thick undoped ZnO film presented in the coordinates $(\alpha hv)^2 vs. hv$.



Fig. 4. Absorption spectra of ZnO:B film presented in $(\alpha h\nu)^2 = f(h\nu)$ coordinates.

fraction data.

We observed a blue shift of the absorption edge in ZnO:B films in respect of the undoped one. Based on the optical absorption spectra of ZnO:B films, there were determined the approximate optical bandgaps: $E_g \approx 3.24$ eV, 3.28 eV and 3.38 eV, respectively, for the

TABLE 3. Bandgap expansion and the concentrations of free electrons in ZnO:B films calculated on Burstein-Moss model.

Sample	ΔE_g , eV	$n, \times 10^{19} \mathrm{cm}^{-3} (m^* = 0.24 m_e)$	$(n, \times 10^{19} \mathrm{cm}^{-3} (m^* = 0.35 m_e))$
ZnO:B (1 wt.%)	0.04	0.4	0.7
ZnO:B (2 wt.%)	0.14	2.8	4.9

boron concentrations of 0, 1 and 2 wt.%. The charge-carriers' concentration in ZnO:B films was found to be of the order of 10^{19} cm⁻³. We demonstrate that the 'blue' shift of fundamental absorption edge in ZnO:B films with increasing of impurity concentration is explained by the Burstein-Moss effect.

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