ON THE PHOTOLUMINESCENCE AND OPTICAL PROPERTIES OF ZINC OXIDE THIN FILMS PREPARED BY THERMAL OXIDATION

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Abstract: Zinc oxide (ZnO) thin films were prepared by thermal oxidation of vacuum evaporated metallic zinc films. Some structural investigation, performed by X-ray diffraction technique, showed that films are polycrystalline and have a würtzite structure. We also determined some structural parameters of the films. The optical absorption was studied in the wavelength range from 300 nm to 1700 nm. Photoluminescence spectra at temperatures 293 K and 78 K have been analysed.

Keywords: zinc oxide, thin films, structural characteristics, optical properties, photoluminescence spectra

1. INTRODUCTION

Zinc oxide (ZnO) is an interesting element of this class which attracted considerable attention owing to various applications such as transparent field-effect transistors, energy-efficient windows, transparent electrodes, flat panel displays, solar cells etc. [1-7]. These applications are based on the optical and electrical characteristics of ZnO (high transparency in the visible spectral range of the solar spectrum, wide direct energy bandgap, low electrical resistivity at room temperature, high thermal and chemical stability etc.), which are very suitable for a great number of new applications in modern solid state device technologies, transparent electronics, sensor tehnology, optoelectronics etc. [1, 2, 8, 9]. Several different techniques have been successfully employed to prepare transparent conductive ZnO thin films, such as magnetron sputtering, spray pyrolysis, chemical vapor deposition, sol-gel (spin coating), pulsed laser deposition, molecular beam epitaxy etc. [10].

Some structural and optical [11] properties of zinc oxide thin films prepared by thermal oxidation of zinc metallic films in different conditions were studied.

Some correlations between preparation conditions and structural characteristics of ZnO thin films have been established.

Due to both theoretical interest and technologic importance, the photoluminescence properties of ZnO thin films have been intensively studied in the last years [6, 9, 10].

Zinc oxide is also a potential candidate for the active film in some important modern devices (laser diodes, light-emitting diodes, etc.) due to its large excitonic binding energy (about 60 meV), which ensures an efficient excitonic emission up to room temperature [1, 6].

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2. EXPERIMENTAL

Zinc thin films were prepared by thermal evaporation under vacuum onto optically flat borosilicate glass (Corning 7059) and amorphous SiO_2 substrates kept at room temperature (T=293 K) during film deposition.

The thermal oxidation procedure of zinc thin films consisted of following successive technological steps: (1) a heating in open atmosphere (relative humidity was about 60%), in the temperature range from 300 K to T_{ox} (where T_{ox} denotes oxidation temperature), with a temperature rate of about 6 K/min; (2) an annealing for a certain oxidation time, t_{ox} (t_{ox}=30–120 min) at a determined oxidation temperature (T_{ox}=500–870 K); (3) a cooling from oxidation temperature to room temperature, with a temperature rate of about 10 K/min. We experimentally established that these preparation conditions permit to obtain ZnO thin films having a homogeneous structure, stable stoichiometry and very good adhesion to the substrate surface.

The surface morphology of ZnO thin films was examined by atomic force microscopy (AFM). The scan was carried out in tapping mode.

The reflection and transmission spectra, in vicinity of fundamental absorption band edge {corrected for the effect of the glass substrate [6]}, in the spectral range from 300 nm to 1600 nm were recorded within temperature range from 78 K to 293 K using a Steag ETA Optik computer controlled spectrometer and a Specord UV-VIS-M.40 (C. Zeiss, Jena) spectrophotometer.

The absorption coefficient, α, at temperatures 78 K and 293 K, was calculated from the expression below:

$$\alpha = \frac{1}{d}\ln\left[\frac{\left[(1-R)^4 + 4 + 2R^2\right]^{1/2} + (1-R)^2}{2T}\right] \quad (1)$$

where d is the film thickness and R and T are reflection coefficient and transmission coefficient at normal incidence, respectively.

Photoluminescence (PL) was measured perpendicular to the sample surface at room temperature. For studied films the following preparation conditions were used: oxidation temperature, T_{ox}=750 K; oxidation time was t_{ox}=60 min; film thickness, d=140 nm. The excitation of photoluminescence was performed by using as excitation source the monochromatic radiation (λ=337.4 nm) from N_2 laser emitting pulses at a frequency up to 82 Hz. The incident beam, with a density up to 100–500 W/cm^2 can be attenuated by using a set of calibrated filters.

The PL spectra at temperature 78 K were recorded by a MDR-2 monochromator with a diffraction grating (1200 mm^{-1}) and as detector a photomultiplier has been used.

3. RESULTS AND DISCUSSION

3.1. Microstructural characteristics

For ZnO thin films studied in present paper the following values of main preparation parameters were used: zinc films were deposited by vacuum thermal evaporation, onto glass substrates (the deposition conditions were previously indicated); oxidation temperature was T_{ox}= 700 K; oxidation time, t_{ox}= 30 min; the thickness of ZnO films was about 270 nm.

Typical XRD patterns are presented in Figure 1 for unoxidized zinc film (with thickness d=190 nm) prepared by described method.

Different peaks were indexed and the values of the interplanar spacing, d_{hkl}, were determined and compared with a standard values for ZnO polycrystalline powder.

The XRD pattern of Zn metallic films indicates a poor crystallization of the films. Some structural characteristics of one ZnO thin film are presented in Table 1.

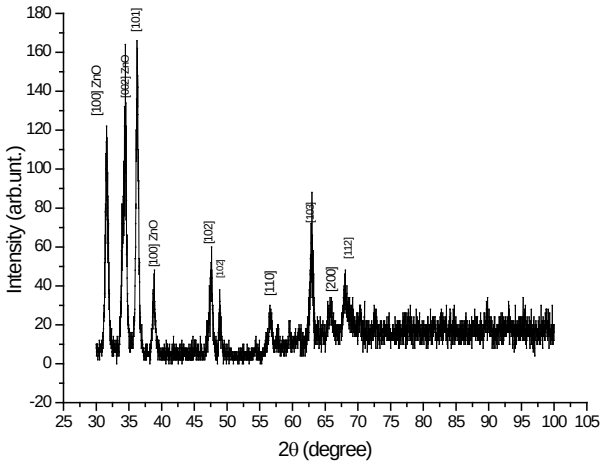

Fig. 1. Typical XRD pattern for ZnO thin film.

Table 1. Values of structural parameters of the investigated ZnO thin films.

Sample	*2θ* [degree]	(hkl)	d_{hkl} (Å)	*D* (Å)	*a* (Å)	*c* (Å)	*L* (Å)
ZNO.042	31.72	(100)	2.819	165	3.259	-	1.913
	34.38	(002)	2.606	145	-	5.213	1.913
	36.20	(101)	2.482	185	-	-	-

θ - Bragg angle; *(hkl)* - Miller indices; d_{hkl} - interplanar spacing of (hkl) planes; *D*-crystallite size; *a*, *c* - lattice parameters of the hexagonal (würtzite) structure; *L*- the Zn-O bond length.

The obtained values of *a* and *c* are in agreement with those of ZnO, given in JCPDS data cards (standard values for polycrystalline powder are: *a*=3.249 Å, *c*=5.206 Å).

The average crystallite size, *D*, can be estimated by means of Debye-Scherrer expression [12-14]:

$$D = \frac{k\lambda}{\beta_{2\theta}\cos\theta} \tag{2}$$

where: *k* denotes the Scherrer's constant, λ is the wavelength of CuK_α radiation (λ = 1.5418 Å), θ is Bragg diffraction angle and $\beta_{2\theta}$ represents the full width at half maximum intensity of the diffraction peak located at angle θ.

All films show the most preferred orientation (002) planes parallel to substrate. The preferred degree orientation decreases with increasing film thickness.

For studied samples, the average crystallite size, determined from Debye-Scherrer formula, ranged between 14.5 nm and 18.5 nm and are higher for films with greater thickness.

The Zn-O bond length, *L*, can be determined from the expression [12-14]:

$$L = \left[\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right] \tag{3}$$

where würtzite structure parameter, u, is given by:

$$u = \frac{a^2}{3c^2} + 0.25 \tag{4}$$

where a and c are lattice parameters.

The relatively small values (for ZnO single crystals, L=2.21Å) for our samples indicate the presence of structural defects (especially oxygen vacancies).

3.2. Optical properties

3.2.1. Absorption coefficient

The films used for the study of the absorption coefficient have been prepared by following technology: zinc films were deposited onto amorphous SiO_2 substrates; oxidation temperature, T_{ox}=835 K; oxidation time, t_{ox}= 110 min.

For the study of the optical characteristics of ZnO thin films, the heat treated samples were used.

The transmission coefficient lies in the range 70%–80% in the visible domain. This high transmission coefficient is due to relatively small roughness of the film surface.

The typical absorption spectra for a ZnO thin film is presented in Figure 2. The dependences α=f($h\nu$) at temperature 293 K consists of an absorption band (α_{max}=5.8×10^5 cm^{-1}) with maximum at 3.343 eV.

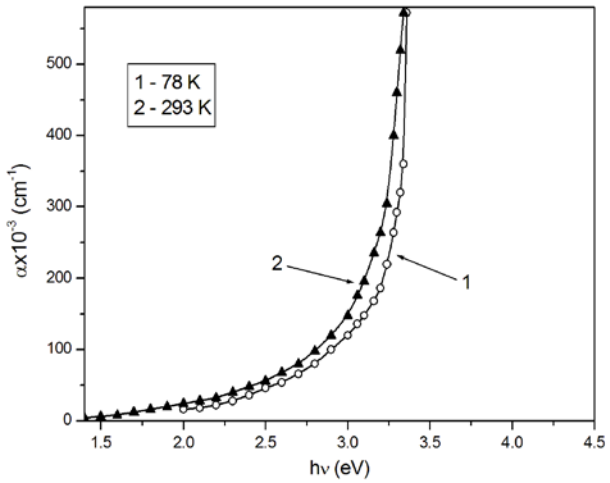

Fig. 2. Typical absorption spectra for a ZnO thin film.

For a studied ZnO thin film, absorption spectra at temperatures 293 K and 78 K are presented in Figure 3. By analyzing these absorption spectra at different temperatures, one can state that the edge of intrinsic absorption band of studied ZnO thin film is located in the energy range from 3.4 eV to 3.5 eV.

The studied ZnO thin films have a high transmission coefficient in visible spectral range (300 nm – 1650 nm).

The Urbach's rule must be inserted [as Eq. (5)], together with some comments. For studied sample, σ_0=3.20×10^{-3} at 293 K and σ_0= 15.5×10^{-3} at 78 K while E_u=4.86 eV at 293 K and E_u=0.434 eV at 78 K. The obtained values show that width of the band tail is greater at low temperature. σ_0 is called the steepness parameter which characterizes the absorption edge shape determined by electron-phonon or/and exciton-phonon interactions.

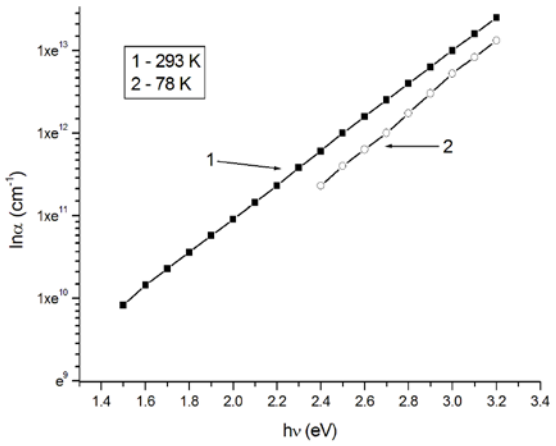

Fig. 3. Absorption spectra for studied ZnO thin film.

3.2.2 Photoluminescence spectra

The following preparation conditions were used for oxidation of Zn metallic films: oxidation temperature, T_{ox}=700 K, oxidation time, t_{ox}=90 min. The zinc films were deposited onto SiO_2 substrates at room temperature by employing a technology described above. The film thickness was d=270 nm.

The typical photoluminescence spectra at temperatures T=293 K and 78 K are shown in Figure 4.

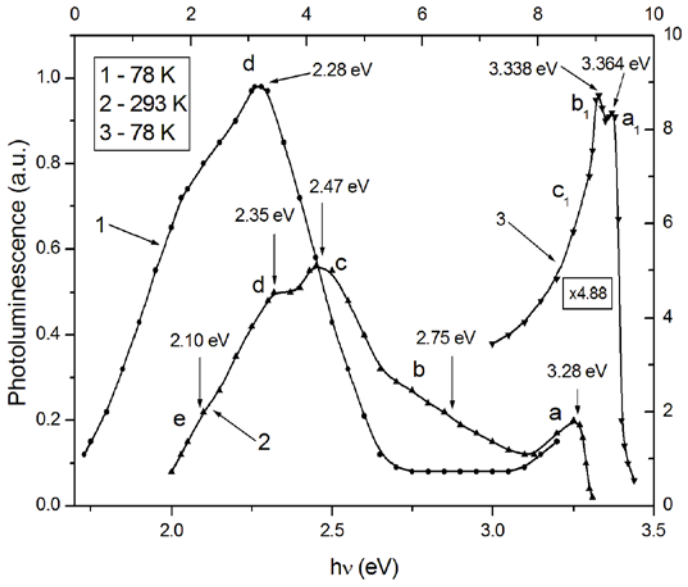

Fig. 4. The typical photoluminescence spectra for a ZnO thin film.

At temperature of 293 K, the spectral dependences of photoluminescence (curve 2) relieve the edge band with a clear maximum at 3.28 eV (a) and a complex band with four sub-bands having an absolute broad maximum at 2.47 eV (c).

This emission bands at 500 nm are determined to the energy level of oxygen vacancies in the energy bandgap.

The luminescence band in visible spectral range consists of four sub-bands (indicated by a, b, c and d): two subbands are located in green range of spectrum at 2.47 eV (c) and 2.35 eV (d), one subband in blue range with a

weak maximum at 2.75 eV and another subband in the orange range of spectrum which has a maximum at 2.10 eV.

As it can be observed by comparison with the absorption spectra and photoluminescence spectra, the (a) band is shifted to smaller energies by 60 meV. This value is in good agreement with Zn-O phonon energy in studied oxide. It can be supposed that band (a) of photoluminescence is obtained as the radiative emission of excitonic transitions with the phonon emission with energy of about 60 meV.

The dominant band in PL spectra which has a maximum at 2.47 eV is explained as the recombination of holes from valence band with electrons from singly ionized level of oxygen vacancies.

The band (b) is considered as the luminescent recombination of an electron from a small-energy-donor-level with a hole from valence band. The (e) band in the orange range is the result of recombination of nonequilibrium electrons from conduction band through ionized oxygen vacancies.

At the temperature of 78 K (curve 1) the structure of two bands is the same in PL spectra. The dominant band from yellow range of spectrum has an impurity nature with the maximum at 2.280 eV (d). Beside, at this temperature, the recombination band of electrons from the conduction band with double ionized oxygen vacancies ($h\nu$=2.10 eV) is present. The edge band at temperature T=78 K could be decomposed into two subbands with maximums at 3.364 eV (a_1) and 3.338 eV (b_1), and a plateau at 3.280 eV (c_1). The PL band with maximum at 3.338 eV is the result of annihilation of free excitons (state n=1) with the emission of optical phonons, because the phonons energy in ZnO films is equal to about 56 meV. The threshold at 3.280 eV can be associated to luminescence of donor-acceptor pair recombination. These peaks can be interpreted as an excitonic transition of bound excitons to neutral donors.

As it can be seen, at temperature of 78 K the PL spectrum is dominated by a strong near-band-edge peak which is positioned at 3.27 eV. This main peak may be attributed to the free-to-bound excitonic emission as peak positions did not change with energy values of excitation source.

There is a smaller peak at about 1.308 eV which is due to structural defects.

It was established that the position of this last peak did not change with the wavelength of the exciting photons.

4. CONCLUSIONS

Zinc thin films were prepared by thermal evaporation under vacuum onto optically flat borosilicate glass substrates kept at room temperature (T=293 K) during film deposition.

The structural investigations show that the phase composition of ZnO films is not influenced by film thickness and used oxidation conditions.

The intrinsic absorption band of ZnO films is formed by free excitons. The width of band gap at the temperature of 78 K of ZnO films is 3.459 eV. The binding energy of electron-gap bound is 67 meV.

The ZnO films show intense photoluminescence in the UV and visible range. The high energy edge of PL spectrum is determined by the luminescence caused by annihilation of excitons from state n=1 bounded to ionized centers.

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