Manufacturing technology, optical and spectral properties of nano-structurized thin ZnO films

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Dependence of cathodoluminescence parameters on the annealing temperature and RF ion etching has been studied for nano-structurized thin zinc oxide films obtained by RF magnetron reactive sputtering. The film structure has been characterized by X-ray diffraction. Thermal annealing and RF ion etching have been found to increase the cathodoluminescence intensity, mainly due to enlargement of the nanocrystallite mean size.

Исследована зависимость параметров катодолюминесценции наноструктурированных тонких пленок оксида цинка, полученных методом ВЧ-магнетронного реактивного распыления, от температуры отжига и обработки ВЧ-ионным травлением. Методом рентгеноструктурного анализа исследована структура пленок. Установлено, что термический отжиг и ВЧ-ионное травление обеспечивают усиление интенсивности катодолюминесценции, главным образом, за счет увеличения средних размеров кристаллитов.

ZnO is a wide-band semiconductor (E_g = 3.37 eV) of n-type conductivity. Due to its good piezoelectric properties, high electric conductance, and transparence in visible and near UV spectral regions, it is used widely in optoelectronics. There are numerous methods to obtain zinc oxide thin films, including thermal deposition [1], reactive sputtering [2], chemical deposition from vapor phase [3, 4], laser sputtering [5, 6], molecular beam epitaxy [7], RF-magnetron sputtering [8–11], RF sputtering [12–16], etc. The RF ion-plasma method is among the best manufacturing techniques of thin oxide films. The method advantages include its suitability for sputtering of high-melting materials, versatility, and low cost. The efficiency of RF-magnetron sputtering is due to a high activity of the gas component molecules that is stimulated by RF plasma action. The ZnO film properties, and in particular, the luminescence parameters, depend heavily on the manufacturing and treatment technology. With the regard for wide application possibilities of that type materials in light-emitting optoelectronic devices, the manufacturing of films with preset optimized parameters takes a special importance. This work is aimed at the study of structure and optical and spectral properties of zinc oxide thin films on the manufacturing and treatment conditions. A special attention is given to manufacturing of films containing nanocrystallites as well as to the nanocrystallite size effect on the film properties.

The thin ZnO films were obtained by RF magnetron sputtering on optical quartz substrates using ZnO targets in argon and argon-oxygen media at the gas pressure of 10^{-3} to $3\cdot10^{-3}$ Torr. The RF oscillator power was 100 W, the target-to-substrate distance 60 mm, the magnet field strength 0.1 T. The crystalline structure was studied using the full-profile data obtained by automated HZG-4A diffractometer intended for examination of polycrystals. The experimental intensity data files were obtained by point-to-point scanning under Cu Kα emission. The crystal structure was determined using CSD software. The analysis included

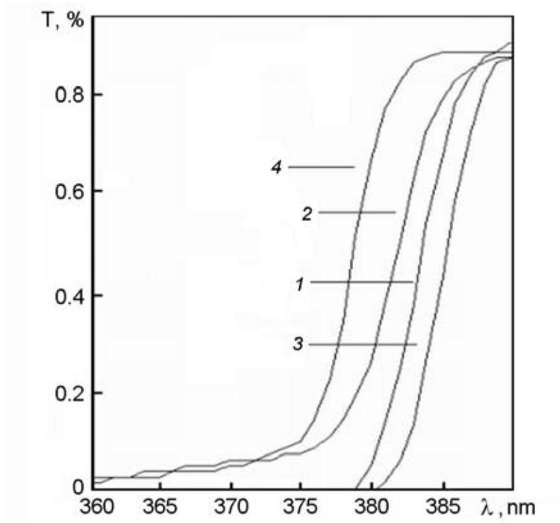

Fig. 1. Optical transmission spectra of 600–620 nm thick ZnO films obtained in various treatment conditions: unannealed (*1*); annealed in air at 600°C for 3 h (*2*); RF-etched for 1 min (*3*); annealed in air at 850°C for 3 h (*4*).

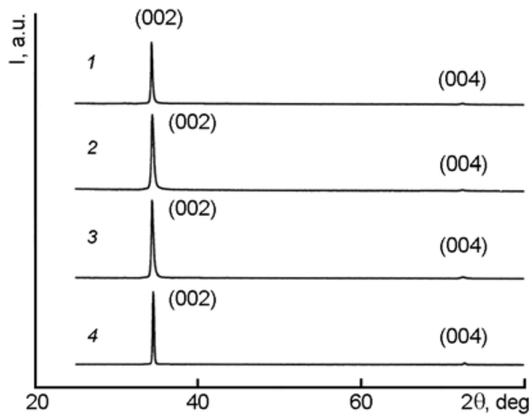

Fig. 2. XRD patterns of thin ZnO films (Cu Kα emission).

the determination of unit cell type by analytical indexing of the diffraction pattern and determination of the unit cell space symmetry group; the structure model development by consideration of the interatomic function distribution; the full-profile refining of the structure positional parameters and the occupancy coefficients for regular point systems to find the isomorphic substitution parameters. As the refining parameters, the atomic coordinates of the basic structure model, isotropic thermal parameters, the unit cell parameters, and the texture parameters were used [17, 18].

The real crystal structure was analyzed considering the XRD pattern profile. The crystallinity extent of the substance was estimated from the block size and the presence of microscale stresses. To consider the polycrystalline film thin structure, the experimental X-ray profile was approximated using the least square method (LSM) by Gauss, Lorentz, and Laue functions, and the reflection integral halfwidth was determined; the experimental profile was expanded into Fourier series and the physical profile was determined by convolution operation; from the physical profile so obtained, the film thin structure (the size of coherent scatter area) was determined. To determine the texture direction of the polycrystalline films, the experimental and theoretical profiles of XRD patterns were reduced to a common scale and the texture indices were determined by iteration using LSM. The nanocrystallite size (L) was calculated as $L = 0.9\lambda/\beta\cos\theta$, where β is the (002) diffraction peak halfwidth; λ, the radiation wavelength; θ, the diffraction angle [19]. The ZnO film cathodoluminescence was examined under excitation with 4 keV electrons at the electron beam current 4 nA. The temperature dependence of the photoluminescence band near the intrinsic absorption edge (λ_{max} = 372–380 nm) was studied under excitation with a LGI-21 nitrogen laser at 337 nm emission wavelength and 9 ns pulse duration.

The as-deposited films show a mirror surface and the transmission coefficient in the visible region of 0.85 to 0.95. The average crystallite size in the films is 15 nm. Fig. 1 shows the short-wave edge of the optical transmission for 600 to 620 nm thick ZnO films obtained in various manufacturing conditions. Thermal annealing is accompanied by the average crystallite size growth from 15 to 60 nm, depending on the annealing temperature (see Table). The films obtained exhibit a high texturization extent in the [001] direction (Fig. 2). The XRD parameters and the unit cell parameters are presented in Table.

The cathodoluminescence spectra of the films comprise the UV exciton emission (λ_{max} = 372 to 380 nm) as well as blue (λ_{max} = 430 to 440 nm) and yellow (λ_{max} = 500 to 560 nm) ones. The luminescence emission depends significantly on the film preparation and treatment conditions (Fig. 3). The films deposited in the argon/oxygen mixture medium show essentially no luminescence. Fig. 4 presents the temperature dependence of the UV luminescence band. As the temperature decreases, the emission intensity rises and the band maximum is shifted towards shorter wavelengths. The luminescence activation energy $E_a \approx 0.08$ eV, as calcu-

Table. Structure parameters of the films

Film No.	Lattice parameters of ZnO films on quartz		Crystallite size, Å	Film No.	*h k l*	2θ (exper.)
	Parameter	Value				
1	*a* (Å)	3.2547	150	1	0 0 2	34.4050
	c (Å)	5.21451				
	Deviation from main optical axis, deg	0.017			0 0 4	72.7140
2	*a* (Å)	3.2504	280	2	0 0 2	34.4020
	c (Å)	5.2112				
	Deviation from main optical axis, deg	0.15			0 0 4	72.7060
3	*a* (Å)	3.2462	140	3	0 0 2	34.4000
	c (Å)	5.2102				
	Deviation from main optical axis, deg	0.0254			0 0 4	72.5500
4	*a* (Å)	3.2496	600	4	0 0 2	34.3070
	c (Å)	5.2005				
	Deviation from main optical axis, deg	0.145			0 0 4	72.6220

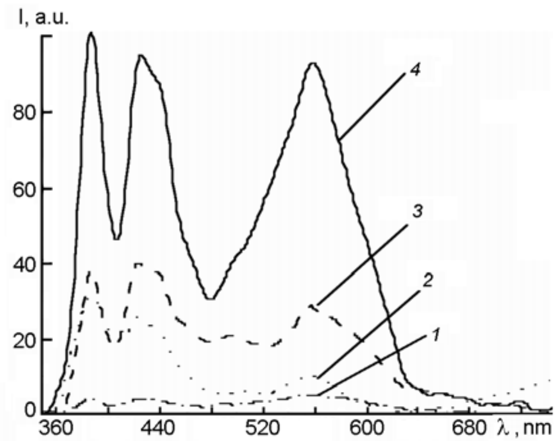

Fig. 3. Cathodoluminescence of thin ZnO films. Notation as in Fig. 1.

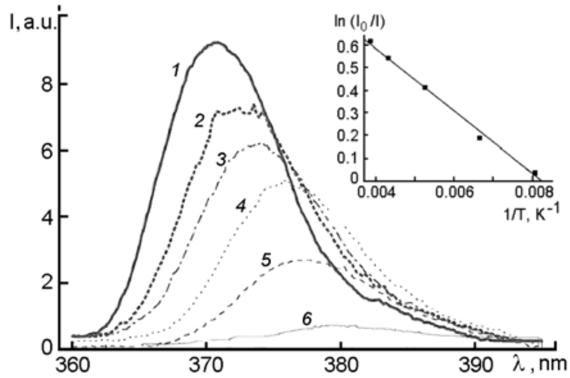

Fig. 4. Temperature dependence of UV photoluminescence band of a 0.6 μm thick film annealed in air at 850°C for 3 h (film No.4). Temperature values (K): 105 (*1*), 150 (*2*), 190 (*3*), 232 (*4*), 285 (5), 317 (*6*).

lated from the $\ln(I_0/I)$ dependence on $1/T$ (see inset in Fig. 4).

The green cathodoluminescence band with a maximum at $\lambda = 500$ nm is associated with oxygen vacancies V_0 in the form of F^+ centers [21, 22]. The blue band in the 430–440 region is due to acceptors, i.e. zinc vacancies V_{Zn} that are formed in the presence of excess oxygen in the zinc oxide crystal lattice. The UV emission at 372–380 nm is due to radiative recombination of bound excitons. The exciton peak shift towards lower energies is explained by the fact that as the temperature rises, an expansion of the crystal lattice occurs and the amplitudes of atomic oscillations about the equilibrium position are enlarged, than, in turn, results in narrower band gap and a change in the exciton spectrum. For more detailed consideration of the exciton emission, the photoluminescence measurement temperature should be lowered down to liquid helium range, especially as the exciton bands in the films are as a rule rather wide and are shifted as compared to those in crystals because of the substrate influence [23]. A high annealing temperature (850°C), films with a bright cathodoluminescence are obtained. This fact is explained by a good polycrystallinity of the films and large grain sizes. At low annealing temperature, the fraction of quasi-amorphous material is rather high and the crystallites are much smaller. Moreover, in this case, the concentration of intrinsic structure defects increases.

Thus, the results obtained evidence a substantial dependence of the cathodoluminescence intensity in ZnO films on the annealing temperature. The films of highest perfection with bright cathodoluminescence are obtained using the high-temperature annealing (at 850°C). Thus, the cathodoluminescence yield can be concluded to increase as the crystallite size rises. It is to note also that, basing on the technology developed, it is possible in principle to obtain the films with pre-specified crystallite size. This makes it possible, on the one hand, to study the quantum dimensional effects in nanocrystallites, while on the another hand, to modify purposefully the properties of thin zinc oxide films taking into account the practical application thereof. The short-term RF etching of the films with high-energy (1 keV) argon ions has been found to increase also the luminescence intensity due to increased number of intrinsic defects.

This work has been done under financial support of the Ministry for Education and Science of Ukraine.

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Технологія одержання та оптико-спектральні властивості наноструктурованих тонких плівок ZnO

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Досліджено залежність параметрів катодолюмінесценції наноструктурованих тонких плівок оксиду цинку, отриманих методом ВЧ-магнетронного реактивного розпилення, від температури відпалу та обробки методом ВЧ-іонного травлення. Методом рентгеноструктурного аналізу досліджено структуру плівок. Встановлено, що термічний відпал та ВЧ-іонне травлення забезпечують підсилення інтенсивності катодолюмінесценції, насамперед за рахунок зростання середніх розмірів нанокристалітів.