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Optical spectroscopy of thin zinc oxide films doped with copper

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The results of a comparative study of the optical properties of the thin films of zinc oxide ZnO, taking into account the influence of their copper doping, are presented. Using the experimental spectra of optical transmission, spectral dependences of the refractive and extinction index of the studied material, as well as components of complex dielectric permittivity constant, were calculated. The revealed features of the obtained dispersion curves are associated with the behavior of the impurity injected into the ZnO matrix.

Keywords: zinc oxide, optical transmission, refractive index, dielectric permittivity.

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1. Introduction

Transparent conducting metallic oxides have become a subject of investigations thanks to their unique physical properties and potential application for the development of micro- and nanoelectronic devices and display units. An essential practical application of these materials is based on significant specific resistance and high visible transmittance. Transparent metallic oxides include, in particular, such compounds as indium tin oxides, zinc oxide, cadmium oxide, etc. Zinc oxide semiconductor as piezoelectric and optical fiber material has practical application potential as functional gas sensor components, surface acoustic devices, transparent electrodes and solar cells [1–4]. High optical band gap values ($\sim 3.3\,\mathrm{eV}$ at room temperature) and exciton binding energies ($\sim 60\,\mathrm{meV}$) allow to address ZnO as a material for creation of next generation ultraviolet-band optoelectronic equipment and phosphors for color display units.

For many of the applications mentioned above, controllability of physical parameters of ZnO thin-film structures, for example, by means of alloying, is essential. In this case, copper alloying additives are more efficient, because copper is a quickly diffusant impurity in a semiconductor that causes modifications of crystalline structure and physical properties, for example, surface state energy parameters as well as optical properties [5–7]. The latter provide additional information on energy structure of optically active faults which is of high practical interest. The purpose of this study is to investigate the behavior of optical constant spectra of undoped ZnO copper doped (ZnO : Cu) thin films.

2. Materials and research methods

Zinc oxide thin films were deposited on uncoated design glass substrates by reactive cathode sputtering method. Zinc was used as the target; and it was possible to produce the studied films with high light transmission level within a single process cycle, while heating to high temperatures was avoided. Injection of copper dopant into the target in atomic concentration about 1% allowed to achieve the required doping level of the produced films.

Spectrophotometric measurements were carried out within $\lambda = 300-900\,\mathrm{nm}$ using SF-2000 optical instrument. Optical constants were determined by means of transmittance measurements using a converter method [8–10]. All measurements were performed at room temperature.

3. Experimental findings and discussion

Synthesized films demonstrated high transmittance (75–80%) up to about 750 nm (Figure 1,2). In the transmission region, transmittance spectrum form $T(\lambda)$ (λ is the incident radiation wavelength) in the long-wavelength range for the studied ZnO films was considerably distorted by interference effects due to multiple reflection of incident radiation which also indicated that the synthesized film was uniform. With uniform film thickness, interference effects result in standard transmittance spectrum with consecutive alternation of maxima and minima.

In high absorption region, interference effects disappear, while maxima and minima envelopes $T_{\mathrm{M}}(\lambda)$ and $T_{\mathrm{m}}(\lambda)$ converge to a single curve for undoped and doped samples.

It has been found before that the observed interference fringes at weak absorption of the studied film may be used to determine its optical properties provided that the film is deposited on a substrate with sufficient transparency and thickness which is several orders greater. Spectral dependence is of the refraction index in the long-wavelength region for uniform thin film deposited on a transparent substrate within the interference region is calculated using the following expression (see [8]):

$$n(\lambda) = \sqrt{N + \sqrt{N^2 - n_s^2}}, \qquad (1)$$

where the following expression is valid for medium and weak absorption region

$$N = \frac{2n_s(T_M - T_m)}{T_M T_m} + \frac{n_s^2 + 1}{2}. \qquad (2)$$

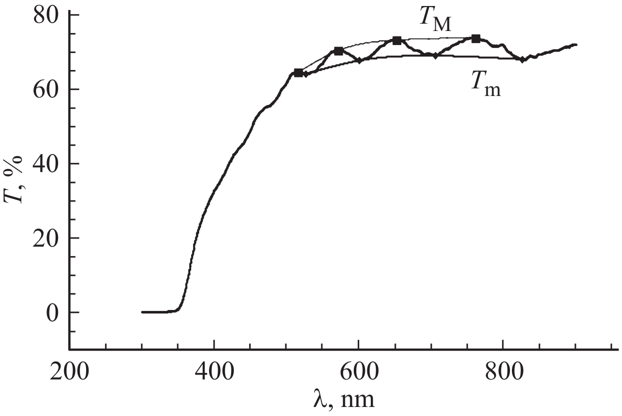

Figure 1. Transmittance spectra $T(\lambda)$ of undoped ZnO film: $T_M(\lambda)$, $T_m(\lambda)$ are interference maxima and minima envelopes, respectively.

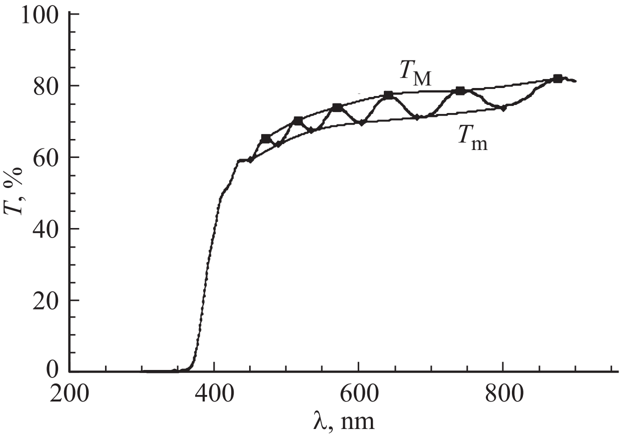

Figure 2. Transmittance spectra $T(\lambda)$ of copper-doped ZnO film: $T_M(\lambda)$, $T_m(\lambda)$ are interference maxima and minima envelopes, respectively.

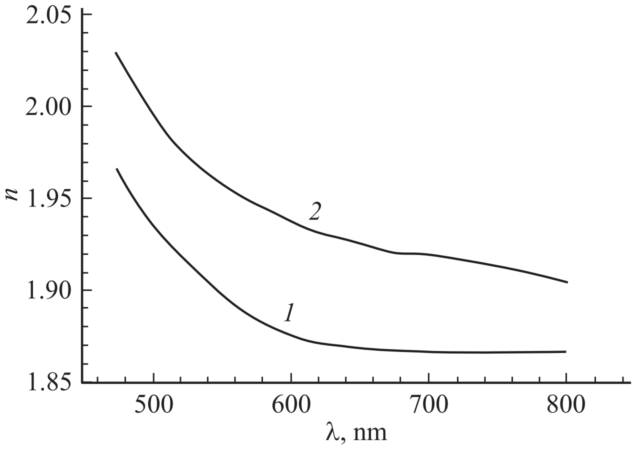

Figure 3. Design spectral dependences of the ZnO film refraction index (curve *1*) and ZnO : Cu (*2*).

Here, T_M and T_m are maxima and minima envelopes of the spectral transmittance dependence with the same wavelength, n_s is the substrate refraction index. The latter was calculated using the following expression, taking into account the normalized value dispersion of the substrate transmittance $T_s(\lambda)$ (see [11]):

$$n_s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}. \qquad (3)$$

Numerical values of ns, which is almost constant in the studied spectral range, is equal to 1.52. Beyond the addressed zone, the refraction index is calculated by the extrapolation method. Figure 3 shows refraction index dispersion dependences of the studied samples calculated using equation (1).

According to the review of the given data, the refraction index decreases with an increase in wavelength when transmittance increases. In this case, refraction index for doped films is higher. Thickness of the studied films, taking into account the interference effect, can be calculated using the spectral dependence of the refraction index from the ratio provided in [12]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}, \qquad (4)$$

where n_1 and n_2 are refraction indices for two adjacent maxima and minima at λ_1 and λ_2.

Calculations of thickness d and refraction index n were corrected in accordance with the interference condition in thin films. Absorption coefficient α of the studied films in the studied wavelength region was calculated using the following relationship

$$\alpha = \frac{2.303 \log_{10}\left(\frac{1}{T_g}\right)}{d}. \qquad (5)$$

Here, $T_g(\lambda) = \sqrt{(T_M(\lambda) T_m(\lambda)}$ is the geometrical mean transmittance without interference and with uniform wavelength.

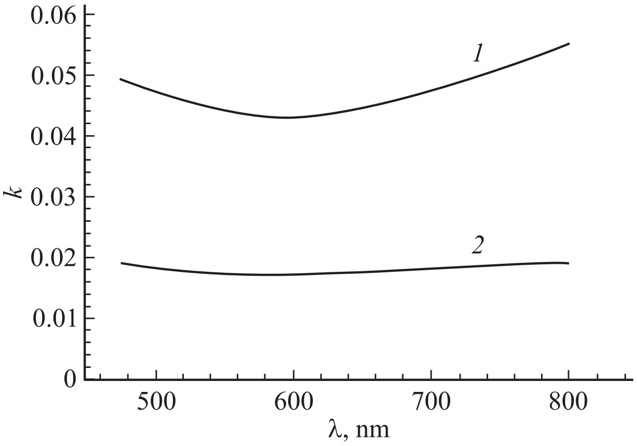

Figure 4. Film extinction coefficient spectra: curve *1* — ZnO, *2* — ZnO : Cu.

The obtained results allowed to calculate spectral characteristics of extinction coefficient $k(\lambda)$ using the equation from [13]:

$$k(\lambda) = \frac{\alpha\lambda}{4\pi}. \quad (6)$$

Study of the behavior of the specified parameter is important for the development of photonic instruments, because it contains the data on the interaction between the material and electromagnetic emission field and characterizes amplitude oscillation attenuation of the electric field strength.

According to the data shown in Figure 4, some growth of k takes place in the region close to the intrinsic absorption edge of the test samples. Loss of light flux in the specified wavelength region caused by dispersion and absorption processes result in reduction of the specified coefficient. It should be noted that the extinction coefficient of the undoped zinc oxide film that has its higher value in the maximum transparency range increases linearly with an increase in the incident radiation wavelength.

The obtained data were used to calculate complex dielectric function components $\varepsilon^* = \varepsilon' - i\varepsilon''$. Real component of dielectric constant ε' indicates the deceleration level of the speed of light in the material, while imaginary component ε'' is associated with the absorption level of the electric field by the studied material due to the orientational motion of relaxing structural components. Figures 5 and 6 show design dispersion dependences for real component $\varepsilon' = n^2 - k^2$ and imaginary component $\varepsilon'' = 2nk$ of ε^*, respectively. Design values of ε' were considerably higher than ε''.

Spectrum behavior $\varepsilon'(\lambda)$ is defined by an electromagnetic wave penetrating inside the studied medium, while dependence $\varepsilon''(\lambda)$ is associated with the electric field energy absorbed by free carriers and also by charge complexes oriented during optical excitation. dielectric constant ε' has higher values in samples doped with 1% Cu. Real component ε^* grows continuously with an increase in photon energy for the doped sample, and the growth is sharper in the high energy region. Loss factor behavior ε'' due to absorption has the same trend as extinction coefficient behavior k.

Comparative assessment of the obtained data shows that ε'' increases with a decrease in photon energy and lower for the doped sample, which is associated with low dielectric loss caused by polarization processes. There is also the influence of the intrinsic defect system formed due to the deviations from the established stoichiometry of the crystal structure. Optical property behavior may be considerably influenced, in particular, by such faults of ZnO lattice as zinc and oxygen vacancies, as well as atoms of these elements in interstices. Moreover, it has been found in [14] that copper atoms injected in ZnO lattice generally substitute zinc atoms and form acceptor type point faults Cu_{Zn} meeting various charge states and donors Cu_i. During optical excitation of these states, complexes similar to exciton systems described by various types of transitions may occur. Copper doping may be also influence the density reduction resulting in the band gap reduction of ZnO : Cu samples [15].

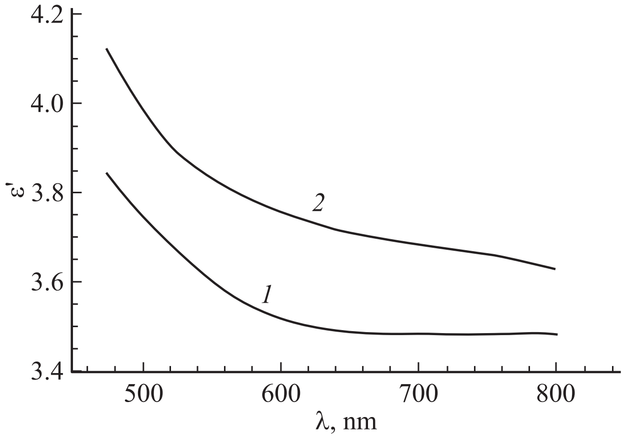

Figure 5. Spectra $\varepsilon'(\lambda)$ of films: curve *1* — ZnO, *2* — ZnO : Cu.

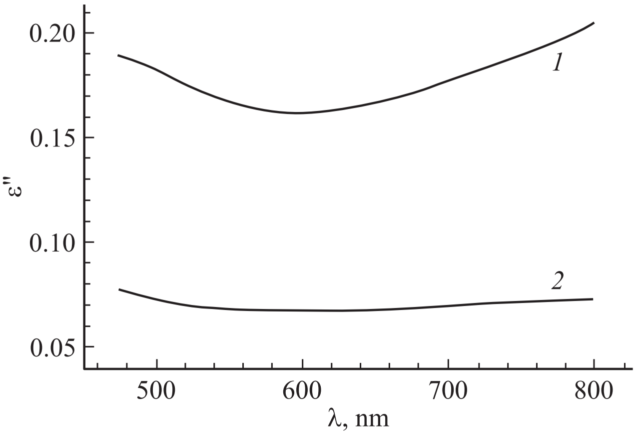

Figure 6. Spectra $\varepsilon''(\lambda)$ of films: curve *1* — ZnO, *2* — ZnO : Cu.

4. Conclusion

Review of the optical measurements in ZnO thin films suggests an important role of the doping factor during injection of copper atoms into the matrix structure of the test samples. This factor has a significant influence on the optical properties of the samples. In this case, when the fault content of the structure increases, the doped samples feature a higher transmittance. The convertor method was used to find the refraction index dispersion, while injection of the copper dopant reduces the refraction index and changes its dispersion in the studied spectral region. Moreover, doping leads to an increase in dielectric constant and decrease in dielectric loss throughout the wavelength range.

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Conflict of interest

The authors declare that they have no conflict of interest.

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