INVESTIGATION OF THE INTRINSIC ABSORPTION EDGE IN NANOSTRUCTURED POLYCRYSTALLINE ZINC OXIDE THIN FILMS

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We have studied the temperature variation of the intrinsic absorption edge of thin polycrystalline films of zinc oxide, obtained by high-frequency magnetron reactive sputtering. We have observed that the intrinsic absorption edge in such films is described by a modified Urbach’s rule. We have calculated the effective frequency of phonons taking part in formation of the absorption edge.

Key words: zinc oxide, thin film, absorption edge, modified Urbach’s rule, phonon frequency.

Introduction. Zinc oxide is a direct-gap semiconductor with bandgap 3.37 eV at room temperature. Due to its high electrical conductivity (usually n-type because of interstitial zinc and oxygen vacancies), piezoelectric properties, and optical transparency, it has become widely used in various optoacoustics and optoelectronics devices. The high exciton binding energy in zinc oxide (∼60 meV) makes it possible to obtain the corresponding luminescence band in the UV region of the spectrum all the way up to a temperature of 550 K [1, 2]. Therefore ZnO is a promising material to use as a basis for designing semiconductor structures emitting in the UV region.

An important factor determining the combination of optical and emission characteristics of a material is the behavior of the intrinsic absorption edge. Studies of this parameter in ZnO single crystals over a broad temperature range (11–878 K) showed that the shape of the absorption edge at $T < 350$ K is described well by the empirical Urbach’s rule:

$$\alpha = \alpha_0 \exp \left[ \frac{\sigma (\hbar \omega - E_0)}{kT} \right] \quad (1)$$

where $\alpha_0$, $E_0$ are constants characterizing the crystal; $\sigma$ is a parameter defining the slope of the spectral curves in the absorption edge region. In this case, the constant $E_0$ can be considered as the bandgap width at $T = 0$ K [3].

Some deviations from Urbach’s rule for zinc oxide single crystals have been observed in the high temperature region [4]. The absorption spectra in the absorption edge region for a number of noncrystalline materials are characterized by the presence of an extended exponential tail, the spectral and temperature behavior of which is governed by the "glassy" or modified Urbach’s rule [5, 6]. According to this rule, the slope of the energy dependences of the logarithm of the absorption coefficient for glasses, in contrast to crystals [7], does not change as the temperature rises and we observe a parallel shift of the indicated curves toward lower energies [6].

From this standpoint, study of the temperature variation of the absorption edge is of special interest in polycrystalline ZnO films, the crystallites of which have sizes ∼10 nm. We may expect that the properties of such materials should be intermediate between the properties of single crystals and glassy materials. This work is devoted to study of the temperature variation of the intrinsic absorption edge for nanostructured polycrystalline thin films of ZnO.

The experiment. Thin films of zinc oxide were obtained by high-frequency magnetron reactive sputtering on substrates of amorphous quartz using ZnO targets under an argon atmosphere with working gas pressure $(1-3) \times 10^{-3}$
torr, high-frequency oscillator power 100 W, distances between target and substrate 60 mm, and magnetic field induction 0.1 T.

We studied the crystal structure using full-profile data obtained on an HZG-4A automatic diffractometer.

To study absorption of light in the UV and visible regions of the spectrum, we used a ZMR-3 mirror monochromator (Russia). The temperature was established and measured within ±0.1 K using an UTREKS system (Institute of Physics, Academy of Sciences of Ukraine).

**Discussion of results.** Immediately after deposition, the films were transparent with a specular surface and transmission coefficient in the visible region of 0.85–0.90. The average size of the nanocrystallites in the films was 15 nm, according to x-ray diffraction. In Fig. 1, we show the transmission spectrum of a ZnO film of thickness 900 nm. A pronounced absorption edge with an exponential "tail" is observed in the 370–380 nm region. The refractive index, calculated using the interference filter method [8] for the region of the spectrum in the vicinity of 550 nm, is equal to 1.962.

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**Fig. 1** Transmission spectrum for ZnO film of thickness 900 nm, obtained at room temperature.

**Fig. 2** Energy dependences of the logarithm of the absorption coefficient for ZnO thin films for the temperatures $T = 395.0$ K (1), 366.9 K (2), 339.2 K (3), 314.3 K (4), and 293.7 K (5).