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EDGE LUMINESCENCE OF ZnO FILMS

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The luminescence spectra of some zinc oxide films near the exciton band have a very wide long-wavelength band. Its intensity increases with the excitation level much more rapidly than the intensity of the exciton bands, which even decreases for some films. It is shown experimentally that the long-wavelength band is not the P-line and is most likely caused by an intrinsic defect or random impurity in the ZnO. An interpretation of this effect based on the Burstein–Moss effect is proposed. A system of rate equations that include a number of parameters is set up for approximate modelling of this effect. These parameters can be chosen so that a numerical solution of this system yields a dependence of the intensity ratio of these bands on the excitation level and (in some cases) a drop in the intensity of the exciton band with increasing excitation level that is close to experiment.

Keywords: *zinc oxide, Burstein–Moss effect, rate equations, shallow levels.*

The near IR luminescence spectrum of some ZnO films consists of two bands. Here we study the intensity dependence of these bands on the level of excitation (pumping). The short-wavelength band (~380 nm) corresponds to exciton emission, while the origin of the long-wavelength band is not fully clear. It has been found experimentally that the intensity of the long-wavelength band increases substantially faster with increasing excitation level than that of the short-wavelength band, while for some films the exciton emission not only falls off relatively, but also absolutely. As far as we know, this effect has not been studied.

The purpose of this paper is to clarify the reason for the anomalous dependence of the intensities on the excitation level that we have observed.

Two types of zinc oxide films were studied: columnar films obtained by pulsed laser deposition on silicon substrates and thin (~40 nm) films produced by magnetic sputtering on quartz substrates with annealing at 750°C in an oxygen atmosphere.

The samples were photoexcited by third harmonic light from a Q-switched Nd:YAG laser (wavelength 355 nm, pulse duration ~10 ns, pulse repetition rate 15 Hz). The luminescence was detected by means of an MDR-23 monochromator with an FEU-79 photomultiplier, the signal from which was fed to a computer. The dependence of the shape of the spectrum on the energy density of the exciting radiation was studied.

An attempt was made to identify the origin of the long-wavelength band. It has been shown experimentally that the long-wavelength band in the luminescence spectra of these films cannot be the *P*-line, since there is no temperature dependence of the spectral separation between the bands studied here. It was also found that the spectral position of the long-wavelength band is independent of the level of excitation, i.e., this band cannot be caused by recombination in an electron-hole plasma. This implies that the long-wavelength band is most likely related to intrinsic defects or random impurities in the ZnO. We have no idea of precisely which defects or impurities are responsible for the observed long-wavelength band. We assume that this long-wavelength band is most likely caused by the presence of a random acceptor impurity in the test films of ZnO–nitrogen atoms at an oxygen site (N_O) [1, 2], which create shallow levels near the valence band (VB). However, it has been shown [3] that the position and behavior of levels in the band gap of ZnO depend strongly on the method and conditions under which the sample was grown. It is possible that this sort of level is created by zinc vacancies (V_{Zn}). This level lies ~0.2 eV above the valence band [4].

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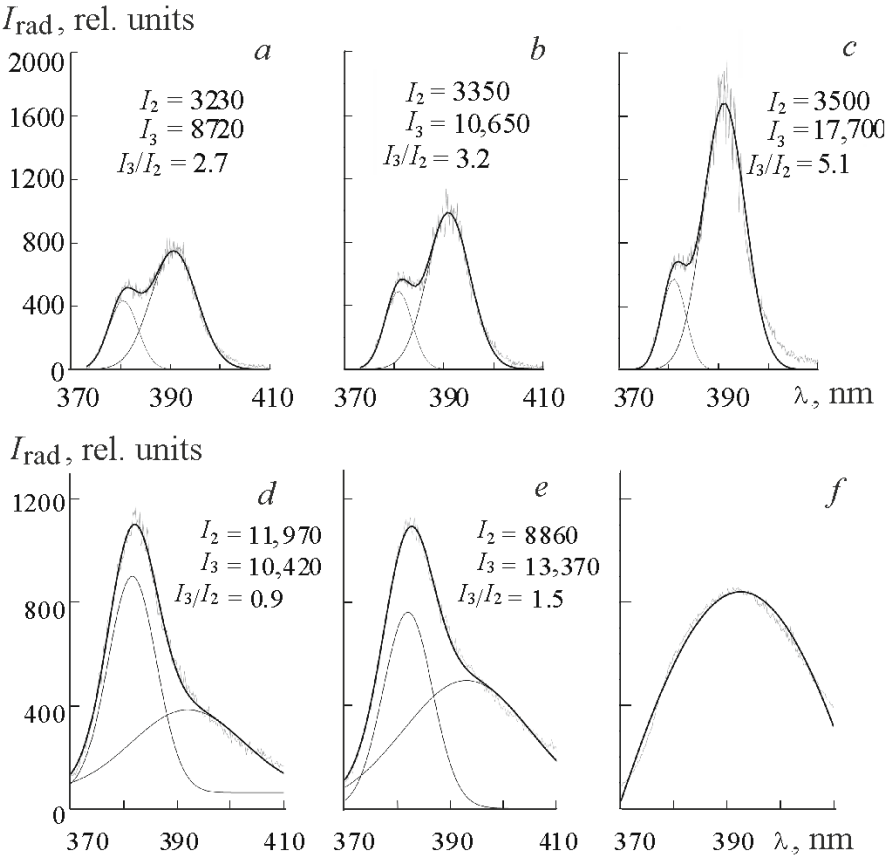

Fig. 1. Luminescence spectra of columnar film No. 76 (a–c) and of a thin film produced by magnetron sputtering and annealing at 750°C (d–f), with decompositions into gaussian components: I_1 = 1.7 (a), 2.2 (b), 2.6 (c), 0.9 (d), 1.2 (e), and 3.4 mJ/cm^2 (f).

Figure 1 shows luminescence spectra of some test films with their resolution into gaussian components; also shown there are the areas under the short- (I_2) and long-wavelength (I_3) components, along with their ratio I_3/I_2 (I_1 is the excitation energy density). For the columnar films, as the excitation energy density is raised the intensity of the band, which is probably related to a random impurity, increases much more rapidly that the intensity of the exciton band. The behavior of the luminescence spectrum of the thin films fabricated by magnetic sputtering is especially surprising. In this case, the intensity of the exciton band does not increase at all as the excitation intensity is raised, but falls off and essentially vanishes at high excitation levels (Fig. 1, Table 1).

A model based on the Burstein–Moss (BM) effect [5] is proposed for interpreting the experimental data. It reduces to an effective increase in the width of the band gap as electrons fill states in the lower part of the conduction band. With pulsed excitation of the luminescence, excitation from both the valence (VB) and conduction bands (CB), as well as from a shallow level in the conduction band, initially takes place as the pulse intensity rises. Then, as a result of the BM effect, excitation from the valence band may cease, while it continues from the shallow level, and the total excitation of the long-wavelength band increases. In accordance with this idea, we have set up a system of rate equations that contains a number of parameters which can be chosen to provide a qualitative model of the experimental data.

For modelling the effect we propose an approximate description of the time evolution of the emission using the following system of four rate equations for the electron concentration in the CV (n_1), the hole concentration at a shallow acceptor level (n_2), the hole concentration in the VB (n_3), and the concentration of excitons (n_4):

$$dn_1/dt = Pe^{-(t-10)2/26.4}(h_1 + \alpha(N_0 - n_2)/N_0) - W_{\text{CB-SL}}n_1n_2 - (W_{\text{CB-VB}} + W_x)n_1n_3\,,$$

TABLE 1. Experimental Results

I_1, mJ/cm^2	I_2	Half width, nm	I_3	Half width, nm	I_3/I_2
Columnar film No. 76					
1.7	3230	7	8720	11	2.7
2.2	3350	6	10,650	10	3.2
2.6	3500	6	17,700	9	5.1
Magnetron sputtering (annealing at 750°C)					
0.9	11,970	10	10,420	20	0.9
1.2	8860	10	13,370	20	1.5
3.4	~0	–	~18,200	~25	–

$$dn_2/dt = \alpha Pe^{-(t-10)2/26.4}(N_0 - n_2)/N_0 + W_{\text{CB-SL}}n_1n_2 + W_{\text{CB-VB}}(N_0 - n_2)n_3 ,$$

$$dn_3/dt = h_1Pe^{-(t-10)2/26.4} - (W_{\text{CB-VB}} + W_x)n_1n_3 - W_{\text{SL-VB}}(N_0 - n_2)n_3 ,$$

$$dn_4/dt = W_xn_1n_3 - Rn_4 - DFn_2n_4 - DE(N_0 - n_2)n_4 .$$

Here t is time (ns); the n_i are the concentrations (10^{18} cm^{-3}); $Pe^{-(t-10)^2/26.4}$ is the pump intensity (the time factor corresponds roughly to the experiment) and the parameter P corresponds to the excitation levels in a range from fractions of, to several, mJ/cm^2; N_0 is the total number of shallow levels; $W_{\text{CB-VB}}$, $W_{\text{SL-VB}}$, and $W_{\text{CB-SL}}$ are the rates of electronic transitions from the CB to the VB, from the shallow level (SL) to the VB, and from the CB to the SL, respectively; W_x is the rate of exciton formation; R is the exciton recombination rate; DF and DE are quantities that determine the rate of recombination of excitons on the random impurity; a is a coefficient that takes into account the difference in the efficiencies of absorption of the pump light into the CB from the SL and from the VB; and, the coefficient $h_1 = 1$ as long as the electron concentration in the CB is such that the effective width of the band gap is smaller than the photon energy (hν) of the exciting radiation (the threshold for the BM effect $n_1 = Q$) and $h_1 = 0$ otherwise.

This system of equations was solved by the Runge–Kutta method. A Mathcad program was set up for this. It calculates the time dependences of n_1, n_2, n_3, and n_4, as well as that of a quantity proportional to the exciton emission intensity $I_2 = \sum_i n_4^i$ and the emission in the transition from the CB to the SL, $I_3 = \sum_i n_2^i n_1^i$. In these expressions the sums are taken over all the subintervals employed to calculate the entire time interval. The calculations were done for a set of parameter choices. It was found that the ratio I_3/I_2 rises with increasing pump intensity only if the threshold Q for the BM effect is exceeded during the pump pulse.

For $\alpha = 0.85$, $Q = 0.84$, $N_0 = 1$ and initial conditions $(n_1)_0 = 0.49$, $(n_2)_0 = 0.42$, $(n_3)_0 = 0$, $(n_4)_0 = 0$, the calculations yielded the following: $W_{\text{CB-SL}} = 3.4$, $W_{\text{CB-VB}} = 155$, $W_{\text{SL-VB}} = 4.5$, $W_x = 230$, $R = 2.5$, $DF = 250$, $DE = 120$, $P = 10/20$, $I_2 = 3031/1577$, $I_3/I_2 = 25.557/65.981$. For the chosen parameters, an increase in the excitation level by a factor of two leads to an increase by a factor of ~2.6 in the ratio of the intensities of the long-wave and exciton bands and to a decrease by a factor of ~1.9 in the intensity of the exciton band. These results are in qualitative agreement with the experiments.

We have, therefore, shown that the anomalous pump dependence of the intensities of these emission bands in ZnO films arises from the Burstein–Moss effect.

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