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Laser deposition of ZnO films on silicon and sapphire substrates

A.N. Zherikhin, A.I. Khudobenko, R.T. Williams, J. Wilkinson,
K.B. User, Gang Xiong, V.V. Voronov

***Abstract*. Laser deposition of zinc oxide films is studied. An intermediate screen is used to prevent microparticles formed during laser ablation of the target from falling on the film. The effect of deposition conditions on the morphology of the film, its electrical properties and crystal structure is studied. It is shown that the laser deposition technique can be used to obtain films of both types. The resistivity of the films was 0.07 Ω cm for films with the *n*-type conduction and 0.08 Ω cm for films with the *p*-type conduction. The photoluminescence studies of the films have shown that stimulated radiation is generated in the films under pump intensity exceeding 6 MW cm^{-2}.**

Keywords: *laser deposition, zinc oxide, sapphire substrate, induced emission.*

1. Introduction

ZnO is a direct-band-gap semiconductor with an energy gap of about 3.3 eV at room temperature [1]. This material is used in piezoelectric devices [2] and optical waveguides [3]. Thin films of zinc oxide are used as transparent conductive coatings [4, 5]. ZnO has a high exciton binding energy (60 meV at room temperature [6] as against 28 meV for GaN). For these reasons, ZnO is seen as a prospective material for near-UV and blue semiconductor lasers [6 – 10].

It is not possible to fabricate a semiconductor laser without developing a technique for producing films made of the appropriate material. Several techniques such as molecular beam epitaxy [8], magnetron sputtering [11, 12], chemical vapor deposition [13] and pulsed laser deposition (PLD) [5, 9, 14 – 17] have been used to deposit zinc oxide films. PLD has a number of advantages compared to other methods, such as deposition under a relatively high partial pressure of oxygen [9], a lower temperature of film crystallisation because of high particle energy in laser plasma, and easy incorporation of dopants into films [18]. PLD also has certain drawbacks, the most significant of these being the formation of drops and microparticles during laser ablation of the target [19]. During deposition, microparticles get implanted in the film, which naturally causes a deterioration of the film quality.

To overcome this problem, a screen should be placed between the target and the substrate. In this paper, we determine the parameters of zinc oxide films obtained by laser deposition using the intermediate screen. The effect of deposition conditions on the morphology of the films, as well as their crystallographic, optical and electrical properties, is studied.

2. Experimental

ZnO films were deposited in an evacuated stainless steel chamber. A turbo molecular pump was used to evacuate the chamber to a pressure of 2×10^{-6} Torr. ZnO films were deposited on monocrystalline 1×1-cm Si [001] and 0.5×0.5-cm sapphire [0001] substrates. We used a metal Zn target (99.99 % purity). A Nd : YAG laser ($\lambda = 1.064$ μm, pulse duration $\tau = 15$ ns, pulse repetition rate $f = 10$ Hz) was used for target ablation. The laser radiation with an energy density of about 1 J cm^{-2} on the target surface was focused by a lens with focal length of 40 cm. The target was rotated at 4 rpm to ensure a uniform processing of the target surface and to eliminate cumulative ablation effects. The target – substrate distance was 50 mm. The substrate was placed on a heater whose temperature could be varied from 100 to 600 °C, and maintained with accuracy not worse than ±5 °C. ZnO films were deposited in a buffer gas. For this purpose, pure oxygen at various pressures ranging from 0.1 to 50 mTorr was used. To obtain *p*-type conducting films, we used a mixture of nitrogen and oxygen at a pressure of 30 mTorr, and the nitrogen partial pressure was varied from 5 to 20 mTorr.

As mentioned above, we used a screen to prevent formation of drops on films during deposition (Fig. 1). A stainless steel screen of thickness 0.25 mm and size half that of the substrate was placed at the mid point between the target and substrate. One can see from Fig. 1 that the trajectory of microparticles that could reach the substrate surface was intercepted by the screen so that no drops were formed on the substrate. Zn atoms and ions reached the substrate due to scattering in buffer gas (dashed curve in Fig. 1). Because only scattered atoms (or ions) could reach the substrate, the process of film growth could be different from the conventional PLD growth without a screen. For

A.N. Zherikhin, A.I. Khudobenko Institute of Laser and Information Technologies, Russian Academy of Sciences, Pionerskaya ul. 2, 142190 Troitsk, Moscow region, Russia;
e-mail: zher@laser.ru; kai@hotmail.ru;
R.T. Williams, J. Wilkinson, K.B. User, Gang Xiong Department of Physics, Wake Forest University, Winston-Salem, NC 27109, USA;
V.V. Voronov A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia

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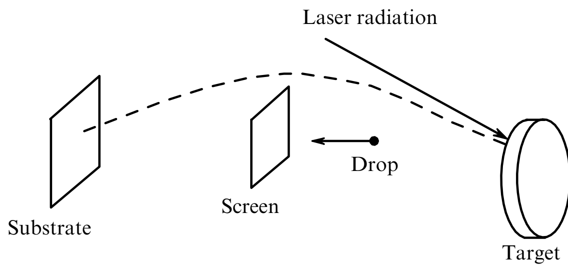

Figure 1. Scheme of the deposition process.

this reason, we studied the properties of zinc oxide films obtained by this technique.

The thickness of the ZnO films was measured with a MII-4 microinterferometer. The crystal structure of the films was studied by the X-ray diffraction method using a copper anticathode source (the Cu 0.15418-nm K_α line) with the filtration of the radiation by a graphite monochromator or a Ni filter. The morphology of films was investigated using an atomic force microscope (AFM) and a tunneling microscope (STM), as well as their photoluminescence. We used the third harmonic of a Ti : sapphire laser ($\lambda = 265$ nm, pulse duration $\tau = 300$ fs, pulse repetition rate $f = 10$ Hz) for excitation of luminescence. Laser radiation was focused on the film surface, the maximum excitation intensity being 800 MW cm^{-2}. We investigated the luminescence spectra with a 600 lines mm^{-1} grating and the luminescence decay with a streak camera with a time resolution of 30 ps. All measurements of luminescence were performed at room temperature.

We investigated the influence of deposition and annealing conditions on the properties of films, and observed thinning of films during annealing at temperatures higher than 500 °C both in vacuum and at relatively low oxygen pressures ($P_O < 500$ mTorr). At present, we do not have an appropriate explanation of this phenomenon because, according to the literature, zinc oxide should be chemically stable under conditions of our experiments (its thermal decomposition can occur only at temperatures exceeding 1000 °C [20]) and cannot sublimate (the only possible phase transition occurs at the melting point of ZnO, i.e., at 1975 °C [1]). Due to a thinning of films at high annealing temperatures, subsequent annealing measurements were made under an oxygen pressure $P_O = 1$ atm and at a substrate temperature $T_a = 400$ °C. No variation in film thickness was observed under these conditions. The electric resistance of the films was measured by four-probe technique and the type of conduction was determined using the Hall effect.

3. Experimental results and discussion

The first experiments showed that deposition using an intermediate screen makes it possible to prevent the entry of microparticles on the substrate. For comparison, we deposited films simultaneously on two substrates, one inside and one outside of the screen shadow. Microparticles of size ~ 0.1 mm were observed on the substrate placed out of screen shadow. At the same time, both optical microscope and AFM measurements did not reveal any microparticles on the substrate covered by the shadow.

We investigated the dependence of film growth rate on substrate temperature and oxygen pressure. These experiments were carried out only on monocrystalline Si substrates. At any buffer gas pressure P_O less than 500 mTorr, the film growth rate increased with the deposition temperature T_d up to 400 °C and decreased upon a further increase in T_d. The film growth virtually terminated at $T_d = 600$ °C. This experimental result agrees with the results available in the literature (see, for example, Ref. [9]), but a correct explanation for such a dependence has not been obtained so far. Subsequent experiments were carried out at $T_d < 600$ °C, and most results presented in this paper correspond to $T_d = 390$ °C.

The AFM images of ZnO films under various growth conditions are shown in Fig. 2. Figure 2a shows the surface of a film deposited on sapphire substrate at $T_d = 540$ °C and oxygen pressure $P_O = 50$ mTorr. The deposition time was 20 min. One can see that the film has an island structure, the average size of islets being about 1000 nm and the film thickness about 160 nm (measurements were performed with a MII-4 interferometer). Each islet consists of crystallites with an average size of about 50 nm. Figure 2b presents the surface structure of films obtained under the same conditions as Fig. 2a, but with a deposition time of 60 min. The mean film thickness increased to about 800 nm. The average dimension of crystallites increased to 200 nm, and most of the crystallites had a hexagonal shape with the c axis oriented at a right angle to the substrate (*c*-orientation). The roughness of the films was 160 nm (Fig. 2a) and 500 nm (Fig. 2b). Films deposited at $T_d < 400$ °C had a quite different surface morphology (Figs 2 c–e). In this case, the crystallite size decreased down to 30 nm and the roughness down to 15 nm.

We did not observe any significant influence of oxygen pressure on film morphology. It remained almost the same at $P_O = 50$ mTorr (Fig. 2c) and 10 mTorr (Fig. 2d). It was reported in Ref. [14] that high-quality epitaxial films can be obtained at a low oxygen pressure of about 0.1 mTorr. Unfortunately, we could not realise this condition because of a low efficiency of scattering of Zn atoms in the buffer gas resulting in a low rate of the film growth. Annealing of films for an hour at $T_a = 390$ °C and $P_O = 1$ atm led to an increase in the crystallite size to about 80 nm, the roughness of the film surface being about 20 nm (Fig. 2e). The morphology of films deposited on silicon substrates (Fig. 2f) was almost the same as that of films deposited on sapphire substrates.

X-ray diffraction patterns of ZnO films deposited on sapphire substrates are shown in Fig. 3. The diffraction peaks (002), (004) and (006) corresponding to the first, second and third diffraction orders can be distinguished easily. We calculated the positions of most asymmetric peaks, but no peaks were detected. This means that the ZnO films have an axial texture and the *c* axis is perpendicular to the substrate surface. Such a situation is typical for ZnO films and the *c*-oriented films can be obtained by PLD [9, 15], molecular beam epitaxy [8], spray pyrolysis [21] and other deposition techniques. Moreover, *c*-oriented films can be grown even on amorphous glass substrates [21].

Using the positions of three diffraction peaks, we determined the unit cell parameter $c = 0.5259$ nm for ZnO films deposited on silicon substrate and 0.5237 nm for films deposited on sapphire substrate ($c = 0.520661$ nm for bulk single crystal). The error in determining the lattice parameter is about 10^{-4} nm, which corresponds to the measurement of the diffraction peak position with an accuracy of 10^{-3} arc degree.

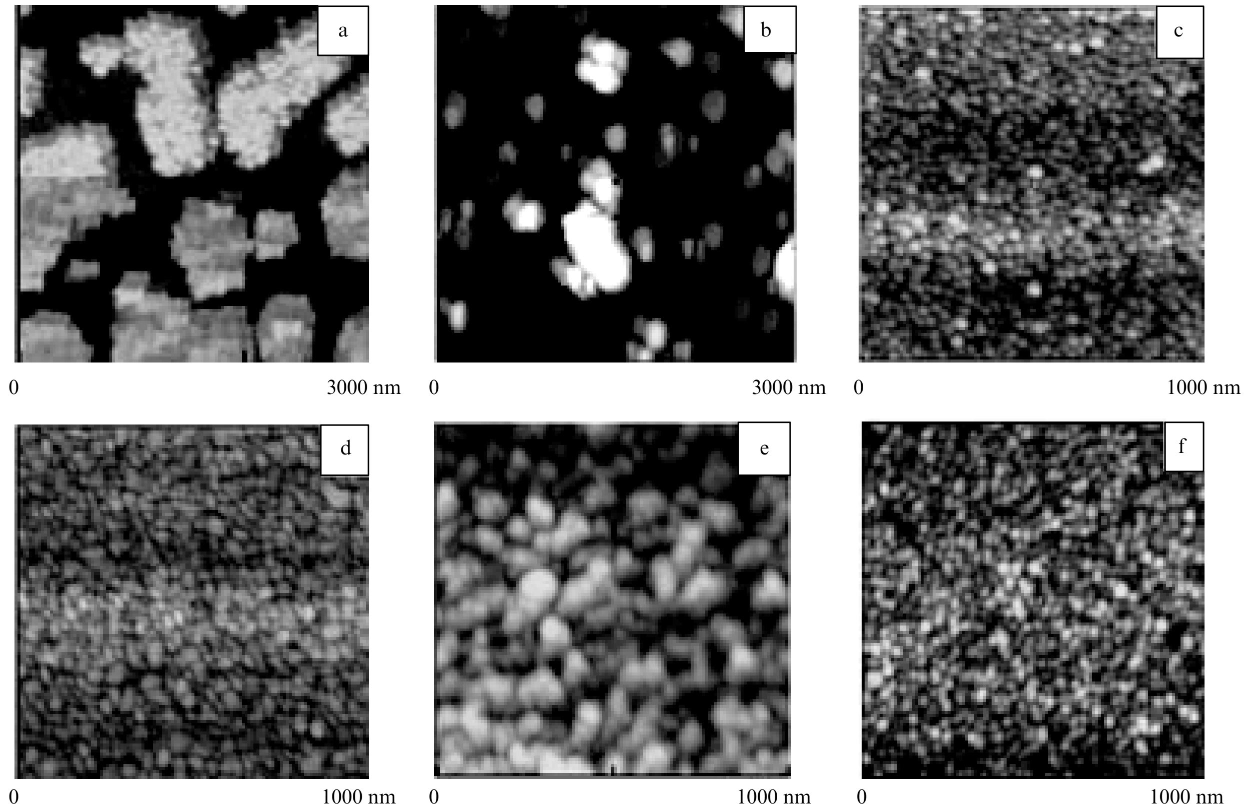

Figure 2. Atomic force microscope images of the ZnO film surfaces on sapphire (a – e) and silicon (f) substrates: (a) $P_O = 50$ mTorr, $T_O = 540\,°C$, depostion time $t_d = 20$ min, (b) $P_O = 50$ mTorr, $T_d = 540\,°C$, $t_d = 1$ h, (c) $P_O = 50$ mTorr, $T_d = 390\,°C$, $t_d = 20$ min, (d) $P_O = 10$ mTorr, $T_d = 370\,°C$, $t_d = 20$ min, (e) $P_O = 10$ mTorr, $T_d = 370\,°C$, $t_d = 20$ min, annealing at $T_a = 390\,°C$ and $P = 1$ atm for 1 h, (f) $P_O = 10$ mTorr, $T_d = 370\,°C$, $t_d = 20$ min.

The full width at the half maximum (FWHM) Ω of the peaks is related to the size D of the region of coherent scattering along the normal to the substrate and micro-deformation $l = \delta c/c$ (in our experiments, the parameter l was averaged over the entire volume of the film) [22]:

$$\Omega^2 = \omega_0^2 + \omega_d^2 + \omega_l^2,$$

$$\omega_d = \lambda_X/(D\cos\theta), \tag{1}$$

$$\omega_l = 4l\tan\theta,$$

where ω_0 is the instrumental function width; λ_X is the X-ray wavelength, and θ is the diffraction angle. Because the diffraction pattern contains three diffraction peaks, we can determine both parameters D and l from formulas (1). The rocking curves were recorded for the (002) peak of the films. Similar curves were also recorded for the (006) peak of the sapphire substrate. Table 1 shows the results of processing of the diffractograms.

In our experiments, D is determined by the size of crystallites in the direction normal to the substrate. Because the thickness of films on silicon and sapphire substrates is 200 nm, it can be concluded that films consist of several layers of crystallites. In the case of silicon substrate, the

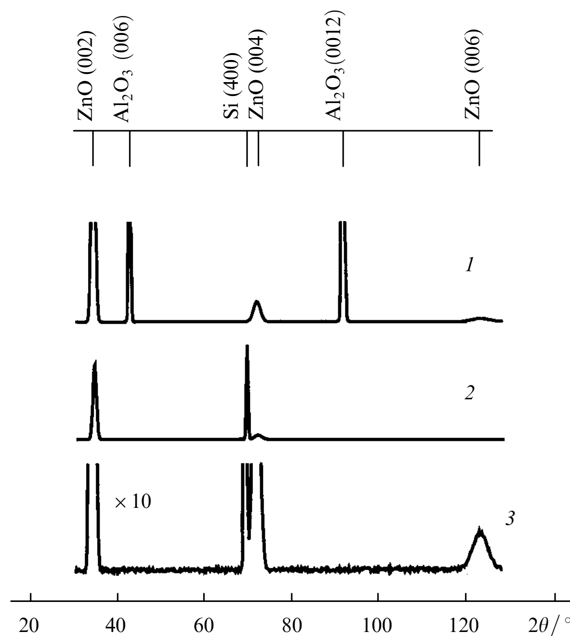

Figure 3. $\theta - 2\theta$ diffraction patterns of ZnO films on sapphire (*1*) and silicon (*2, 3*) substrates.

Table 1.

Sample	D/nm	$l = \delta c/c$	Rocking curve halfwidth/°
ZnO/Si [001]	50	10^{-3}	3
ZnO/Al_2O_3 [0001]	22	4.3×10^{-3}	1.2
Al_2O_3 [0001] (006)			0.08

average number of layers is four while for a sapphire substrate the number can increase to nine. It should be mentioned that monocrystalline silicon with orientation [001] and sapphire with orientation [0001] are not quite suitable for epitaxial growth of ZnO films because of a considerable mismatch of lattice parameters. For the ZnO/Si system, the mismatch is 31 %, while for the ZnO/Al_2O_3 system, the mismatch is 18 % [23]. Moreover, the ZnO and Si lattices have different symmetries.

Consequently, the data obtained by X-ray structural analysis can be interpreted as follows. Since films deposited on both types of substrates consist of several layers of crystallites, the layer closest to the substrate has a highly deformed unit cell because of a considerable mismatch of the lattice parameters. The cell parameters approach the values of parameters for a single crystal as we move away from the substrate. The difference between the cell parameters gradually decreases at the boundaries between crystallites as we go over from one layer to the next. Because the number of crystallite layers on sapphire substrates is twice that on silicon substrates, the lattice parameters for films deposited on sapphire substrates are closer to the parameter of the free ZnO lattice (single crystal). This also explains the large value of l for sapphire substrates because the value of δc for them is higher than for silicon substrates.

A lower width of the rocking curves for sapphire substrates indicates that the fluctuations in the direction of the c axis for various crystals are about three times smaller than for silicon substrates.

Films deposited in oxygen atmosphere on silicon as well as sapphire substrates had the electron conduction, which is typical of ZnO films [24]. It is known that free electrons appear in ZnO due to the oxygen deficiency because oxygen vacancies play the role of donor impurities [25]. The conduction of the films depended significantly on the conditions under which the films were deposited. The films deposited at $T_d = 540\,^\circ C$ and oxygen pressure $P_O = 50$ mTorr had a resistivity $\rho > 100\ \Omega$ cm (the upper limit of the measuring system). The conduction of the films increased with decreasing T_d or P_O. We deposited films on silicon with $\rho = 0.3\ \Omega$ cm at $T_d = 36\,^\circ C$ and $P_O =$ 50 mTorr and with $\rho = 0.05\ \Omega$ cm at $T_d = 360\,^\circ C$ and $P_O = 10$ mTorr. Such behaviour can be explained easily because the number of oxygen vacancies and hence the concentration of free electrons decreases with increasing temperature. All the films became dielectric after annealing at $T_a = 400\,^\circ C$ and $P_O = 1$ atm. This is due to the same reason, namely, a decrease in the concentration of oxygen vacancies. Likewise, the resistance of zinc oxide films on sapphire substrates depended on the deposition and annealing conditions. The minimum resistivity of the films obtained by us was $0.07\ \Omega$ cm for films deposited at $T_d = 370\,^\circ C$ and $P_O = 10$ mTorr.

In order to obtain zinc oxide films with hole conduction, we should first suppress the electron conduction caused by the oxygen deficiency, and then introduce a sufficient amount of acceptor impurities into the film. According to theoretical estimates, nitrogen is the best candidate [26] among various acceptor impurities (Li, Ag, Cu, etc.). ZnO films with the hole conduction were obtained by magnetron sputtering [11, 12] and by PLD [16, 17]. The technique of simultaneous doping with gallium and nitrogen was employed in Ref. [17], and the films obtained by this method had a resistivity $\rho = 0.005\ \Omega$ cm. N_2O was used as the source of nitrogen in Ref. [17]. In our experiments, we used a mixture of N_2 and O_2 as the buffer gas for obtaining the hole conduction. Deposition was performed under the following conditions: $T_d = 380\,^\circ C$, $P_O = 10$ mTorr and $P_N = 20$ mTorr. After deposition, all the films were found to be dielectric. As mentioned above, the films obtained under these conditions but in the absence of nitrogen had the electron conduction. This means that the introduction of nitrogen suppressed the electron conduction. After deposition, the films were annealed for one hour at $T_a = 400\,^\circ C$ and $P_O = 1$ atm. Measurements revealed that the films acquired the hole conduction after annealing and had a resistivity of $0.08\ \Omega$ cm. It should be noted that a change in the conditions of deposition (partial pressure of gases by 10 % and temperature by 30 °C) led to a sharp increase in the resistivity of the films (by a factor of 50 – 60).

Figure 4 shows the luminescence spectra of ZnO films on silicon and sapphire substrates. The thickness of all films in these experiments was 150 nm. At the same excitation intensity ($I < 1$ MW cm^{-2}), the luminescence intensity of ZnO films on a silicon substrate was two orders of magnitude lower than that of ZnO single crystals and of films on sapphire substrate. The luminescence spectrum of films on a silicon substrate (curve *2* in Fig. 4) consists of two bands at 382 nm and 406 nm. The first band at 382 nm corresponds to free exiton emission and the second band at 406 nm to the electron-hole plasma recombination emission [8].

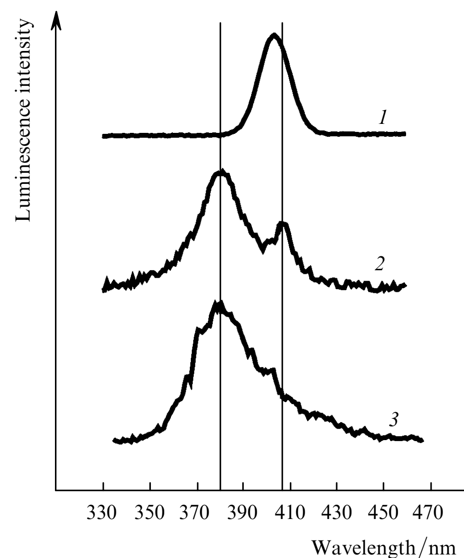

Figure 4. Luminescence spectra of ZnO films on sapphire (*1*) and silicon (*2*) substrates, and of a single crystal (*3*).

The dependence of the luminescence spectra on the oxygen pressure during deposition showed that the intensity of the free exciton band increased with pressure and at $P_O = 50$ mTorr it dominated the luminescence spectrum. Under these conditions, no emission of the electron-hole plasma was observed. Annealing of the films in oxygen atmosphere ($P_O = 1$ atm, $T_a = 400\,^\circ C$) also causes a slight increase (by a factor of about 2) in the free exciton band intensity. Such behaviour can be explained as follows. It is well known that ZnO films contain many various defects

(oxygen vacancies, zinc interstitials, etc.). The presence of defects causes an increase in absorption at the long-wavelength side of the fundamental absorption band where the luminescence band is located [27]. Deposition at high oxygen pressure and annealing in oxygen atmosphere reduce the concentration of defects (at least, it reduces the concentration of oxygen vacancies). A decrease in absorption leads to an increase in the luminescence intensity.

No significant change in the luminescence spectra was detected upon a variation of the deposition temperature. The luminescence intensity decreased at $T_d > 400\,^{\circ}C$, which can be attributed to a decrease in the film thickness under these conditions.

The luminescence spectrum of *n*-type ZnO films deposited on a sapphire substrate is shown in Fig. 4 (curve *1*). This spectrum consists of a single band at 402 nm. The band shifts to the red side with the excitation intensity. According to the assignment proposed in Ref. [8], this band corresponds to the recombination of the electron-hole plasma. A comparison of the luminescence spectra of the films of the same thickness but deposited at different temperatures shows that the luminescence intensity increases with T_d. Annealing of films in oxygen atmosphere also causes a growth in the luminescence intensity by a factor of 3–5. As in the case of silicon substrate, this is also due to a decrease in the concentration of oxygen vacancies.

The intensity and wavelength of the recombination emission band of the electron-hole plasma depend on the excitation intensity I (Fig. 5). The wavelength shift caused by a tenfold increase in the excitation intensity is about 13 nm ($\lambda = 400$ nm for $I = 80$ MW cm^{-2} and $\lambda = 413$ nm at $I = 800$ MW cm^{-2}), which can be attributed to the band-gap renormalisation caused by a high concentration of the excited particles [8]. A nonlinear dependence of the electron-hole plasma recombination band intensity on the excitation intensity I was observed experimentally. The emission intensity increased by 70 times upon a tenfold increase in the excitation intensity from 80 MW cm^{-2} to 800 MW cm^{-2}. The nonlinear increase in the luminescence intensity is typical of stimulated emission. However, further detailed investigations of the luminescence spectrum (its width, mode structure, etc.) should be carried out to obtain a convincing proof that stimulated emission was indeed observed in our experiments.

The time dependence of the luminescence intensity of the *n*-type ZnO film on a sapphire substrate is shown in Fig. 6 (curve *2*). For comparison, the time dependence of the luminescence intensity of a ZnO single crystal obtained under the same conditions of excitation and measurement is also shown (curve *1*). The time resolution of these measurements was approximately 30 ps. The FWHM duration of the luminescence band of the film (Fig. 6 curve *2*) was 35 ps, which coincides with the time resolution of the system. The short decay time of of the ZnO film confirms our conclusion that we observed stimulated emission because the duration of the exciting laser pulse was 300 fs.

The luminescence spectra of the *p*-type ZnO films exhibited substantially different behaviour (Fig. 7). These spectra contained only one band at 390 nm, which corresponds well to the *P*-branch of the exciton–exciton elastic collision band [8]. Under identical excitation conditions, the luminescence band intensity was approximately the same for the *p*- and *n*-type films. As mentioned above, the *p*-type films could only be obtained in a very narrow interval of deposition parameters, and hence we could not determine the influence of deposition conditions on the luminescence spectra of these films. We observed a nonlinear increase in the luminescence intensity with the excitation intensity for both *p*- and *n*-type films. However, the wavelength of the luminescence band of the *p*-type films was independent of the excitation intensity, which is quite natural if this band corresponds to the *P*-branch of the exciton–exciton collision band [8].

4. Conclusions

Thus, our experimental studies have led to the following conclusions.

(i) The formation of droplets and microparticles, which inevitably occurs during laser ablation of targets in the PLD

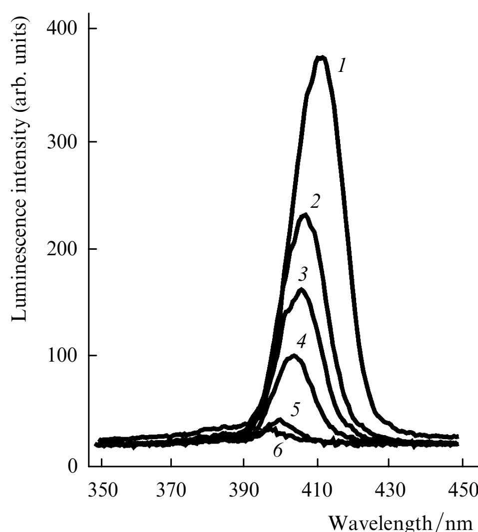

Figure 5. Effect of excitation intensity on the luminescence spectra of ZnO films on sapphire substrate: $I = 800$ (*1*), 500 (*2*), 320 (*3*), 200 (*4*), 130 (*5*) and 80 MW cm^{-2} (*6*).

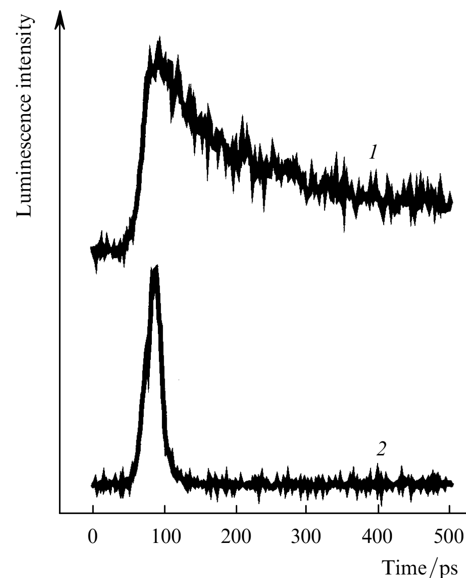

Figure 6. Time dependence of the luminescence intensity of a single crystal (*1*) and a ZnO film on sapphire substrate (*2*).

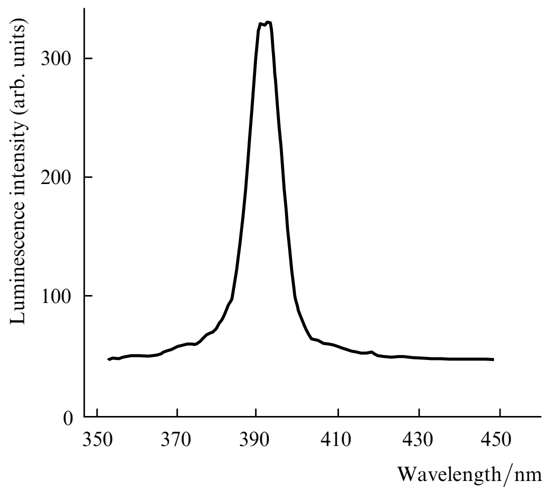

Figure 7. Luminescence spectrum of a p-type ZnO film.

technique, can be prevented by placing an intermediate screen between the target and the substrate.

(ii) Both n- and p-type ZnO films can be produced by the PLD technique. To obtain the p-type conduction, it is expedient to use an $N_2 - O_2$ mixture as the buffer gas.

(iii) ZnO films obtained by PLD technique with intermediate screen demonstrate good photoluminescence properties. A nonlinear increase in the luminescence intensity is observed upon laser excitation.

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