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The change in optical characteristics of ZnO crystals under ruby laser irradiation

I.V. Markevich, V.I. Kushnirenko, A. Baidullaeva, B.M. Bulakh, P.V. Pobirovskiy

V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 45, prospect Nauky, 03028 Kyiv, Ukraine
Phone / Fax: (044) 525-83-44
E-mail: vl_kush@ukr.net

Abstract. The influence of pulsed ruby laser irradiation on luminescence and optical transmission spectra of nominally undoped ZnO single crystals was investigated. Both treatment and measurements were performed at 300 K. The irradiation was found to cause the increase of crystal transmission in absorption edge region and the rise of shortwave wing of exciton luminescence with respect to its longwave one. These changes were accompanied with the rise of electric conductivity. The analysis of obtained results in common with earlier data led to the conclusion that the movement of mobile shallow donors from dislocations to crystal bulk took place under the influence of ultrasound wave excited by laser pulse. The decrease of shallow donor density near dislocations resulted in the shrinkage of c-band state density "tail" in these regions, which caused the shift of the optical absorption edge to the shortwave side.

Keywords: laser irradiation, dislocations, point defects.

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1. Introduction

Pulsed laser irradiation is often used for semiconductor laser pumping. On the other hand, such irradiation is known to influence semiconductor characteristics [1-8], which can result in degradation of the devices. To minimize this effect, it is necessary to elucidate the nature and mechanisms of processes occurring in semiconductor under laser pumping.

One of the most promising materials for UV – blue light-emitting devices, in particular lasers, is zinc oxide. A big advantage of ZnO over widely used GaN is large exciton binding energy (0.06 eV), which enables exciton luminescence to be observed up to 300 K. High efficient lasing action in the exciton luminescence region has been reported for ZnO single crystals [10-14], polycrystalline films [15] and nanowires [16] under electron beam [10, 14] or optical [11-13, 15] pumping in 77 – 300 K temperature range. For optical pumping both one-quantum excitation (Xe laser $\lambda = 364.6$ nm [11] or Nd:YAG laser $\lambda = 355$ nm [15]) and two-quantum one (ruby laser $\lambda = 694.3$ nm) [12, 13] were used. The former excites only near-surface region, while the latter can generate the high density of hole-electron pairs in crystal bulk, which allows homogeneous lasing action to take place in several millimetre thickness crystal [13].

As the lasing occurs in the absorption edge region, one can expect that some distortion of the emission will take place due to partial reabsorption of emitted light by the crystal. Really, the position of the laser emission band and its intensity were found to be strongly influenced by the shift of absorption edge as a result of temperature change or crystal surface treatments [10, 14]. At the same time, optical characteristics of semiconductor can be also changed under action of pumping excitation. Such effect was earlier shown to occur in CdS [9]. In this work, the influence of pulsed ruby laser irradiation on optical characteristics of ZnO single crystals has been investigated.

Fig. 1. ZnO single crystal grown by the vapour phase technique. "c" – crystal region that was treated with ruby laser pulse; "c" and "d" – crystal regions in which optical characteristics were measured.

2. Experimental procedure and results

ZnO crystals were grown using the vapour-phase technique. The crystals were needle shaped, colourless and transparent, with the hexagonal cross-section 0.2 – 0.4 mm^2 and 10 – 15 mm in length (Fig. 1). Photoluminescence (PL) and optical transmission (OT)

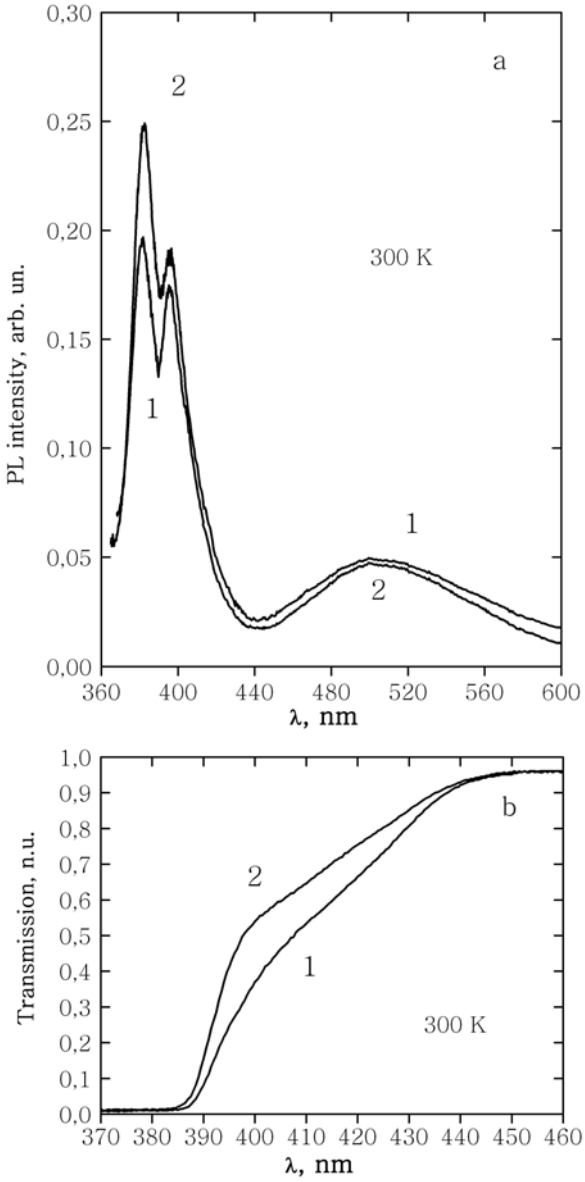

Fig. 2. PL (a) and OT (b) spectra of ZnO crystal N8 measured in "c" region before (1) and after (2) ruby laser treatment.

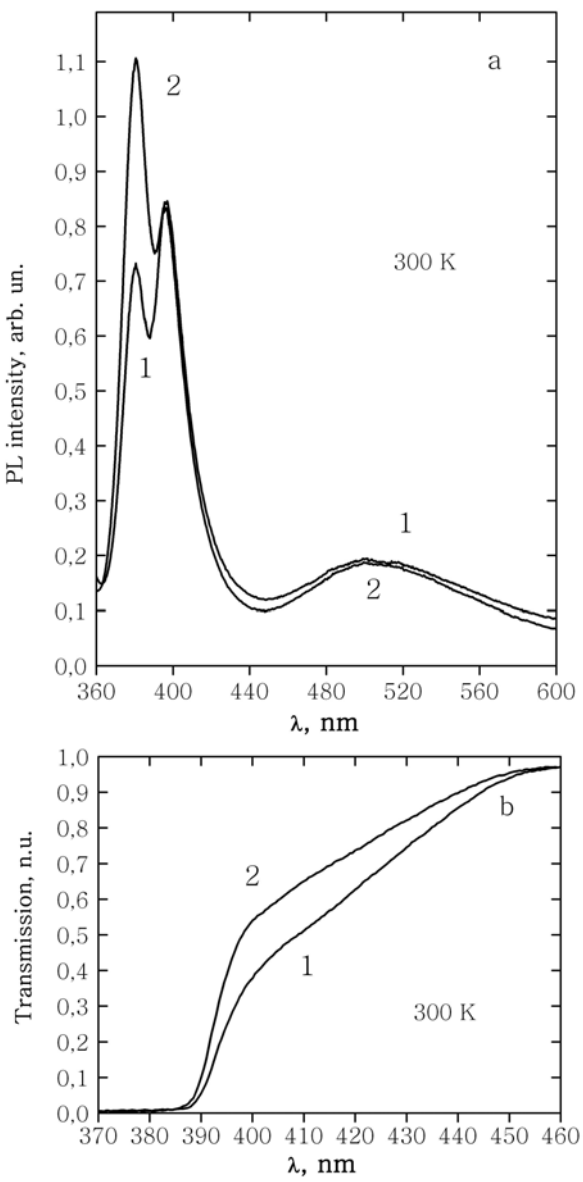

Fig. 3. PL (a) and OT (b) spectra of ZnO crystal N15 measured in "d" region before (1) and after (2) ruby laser treatment.

spectra at 300 K, as well as electrical conductivity in 90 – 400 K temperature range were measured before and after a ruby laser pulse treatment. PL was excited by N_2 laser line λ = 337.1 nm passing through monochromator MDR-12.

In OT spectra measurements, incandescent lamp light was used. For electric measurements, indium electrodes were melted on the crystal ends, the distance between electrodes being 10 – 15 mm. The electrodes were ohmic both before and after laser irradiation. The treatment was performed with 20 ns duration pulses of a multimode ruby laser operating in Q-switch regime. The energy density of radiation was chosen to be 4 – 8 J·cm^{-2}, which was equal or greater than that used for two-quantum pumping [12, 13]. Laser light was focused on the front crystal plane. The diameter of the light spot was about 1 mm. Laser action was followed by a flare, and a crater was observed on the crystal surface after irradiation. The crystal was irradiated in the region "c"; PL and OT characteristics were measured both in "c" region and in "d" one that was about 10 – 12 mm away from the "c" region (Fig. 1). PL spectra were recorded from the front crystal surface.

The results are shown in Figs 2 and 3, respectively. In both cases, the same changes in crystal optical characteristics were observed. More than twenty crystals were investigated.

In PL spectra, exciton bands in UV-light region and the so-called "green" band related to deep centres [16] in the visible light region were present (Figs 2a and 3a).

Exciton luminescence spectra consisted of two distinct peaks and were typical for ZnO single crystals [17]. The peak at $\lambda = 380$ nm is proved to be formed by superposition of the free exciton band Ex and its first phonon replica; the peak at $\lambda = 396$ nm is the second phonon replica [18]. As Figs 2a and 3a show, ruby laser irradiation resulted in the increase of 380 nm peak intensity I_1 with respect to that of 396 nm one I_2; at the same time, any influence of the treatment on the green band shape or intensity was not observed. Transmission spectra of the same samples are shown in Figs 2b and 3b, respectively. One can see that redistribution of I_1 and I_2 values in PL spectrum was accompanied with the change in OT one: after the treatment, the crystal became more transparent in the near absorption edge region. Simultaneously with the changes in optical characteristics, the increase of electric conductivity was observed after the laser irradiation (Fig. 4). The effects were found to be reversible: the initial PL and OT spectra, as well as the value of conductivity restored gradually for several days at 300 K.

It should be noted that, for most of the investigated crystals, the results similar to described above were obtained. At the same time, some samples did not show any change in both optical and electric characteristics under ruby laser irradiation.

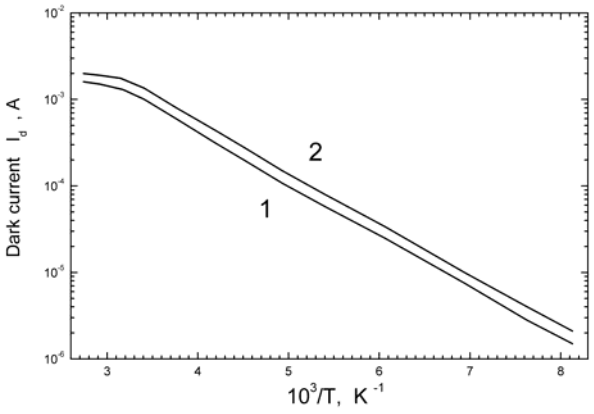

Fig. 4. Temperature dependence of dark current before (1) and after (2) ruby laser treatment.

3. Discussion

A number of effects were found to take place in II-VI compounds under ruby laser pulsed irradiation:

- creation of native defects [1-3];
- photoinduced defect reactions [4];
- multiplication of dislocations and following gettering of point defects by new dislocations [5];
- redistribution of mobile point defects between crystal bulk and near-dislocation regions under the influence of ultrasound (US) wave arising under the laser pulse [8, 9]. It should be noted that such redistribution was also observed in CdS, CdTe and $Zn_xCd_{1-x}Te$ under the influence of sinusoidal US wave [6, 7, 19].

Most likely, described above changes in ZnO crystal optical characteristics result from the later process. Really, creation of native defects should influence the intensity of green PL band that is very sensitive to the density of these defects [17]. Besides, ZnO is known to be highly resistive to radiation damage [20]. Photoinduced defect reactions should occur directly in the irradiated crystal region, while the observed effects took place also when the treated region was far away from that where PL and TO spectra were measured. At the same time, dislocations decorated with mobile shallow donors were recently shown to be responsible for the formation of absorption tail and distortion of exciton luminescence spectrum in as grown ZnO single crystals [21].

The improvement of optical characteristics after ruby laser pulse is the evidence that multiplication of dislocations did not take place in ZnO, which is in accordance with low plasticity of these crystals [17]. Hence, the redistribution of point defects between decorated dislocations and crystal bulk can be supposed. Such effect was earlier found and investigated in detail in CdS [8, 9, 22]. It was shown that shallow mobile donors (Cd interstitials) were gathered by dislocations, and c-band state density tail formed in these regions because of high Cd_i density [22]. Optical transitions of electrons from v-band to this state density tail caused the shift of the absorption edge to longwave side, which resulted in distortion of the edge emission spectrum [23]. The ruby laser pulse was shown to create a tandem of damped US pulses that excited dislocation vibrations in CdS [8]. The latter resulted in the change of shallow donor density in near-dislocation regions, which influenced the c-band state density tail and, so, crystal optical characteristics, the higher dislocation density, the greater this effect [9]. Since ZnO also has the high density of mobile shallow donors Zn_i [17, 24] that decorate dislocations [21, 25], similar processes can be thought to take place in these crystals. The present results can be accounted for by the decrease of shallow donor density in near-dislocation regions because of their replacement to the crystal bulk under the action of US wave created by ruby laser pulse. This conclusion is in accordance with the increase of crystal conductivity after the irradiation and with earlier data for ZnO crystals [21], where the reduction of the extent of dislocation decoration with shallow donors resulted in "correction" of the exciton luminescence spectrum shape. In the absence of ruby laser irradiation, mobile donors return gradually to the dislocations, and the initial characteristics restore. As for ZnO crystals that showed no characteristic changes under the treatment, one can think that these crystals have a low dislocation density.

In conclusion, in nominally undoped ZnO single crystals photoluminescence and optical transmission spectra were measured at 300 K before and after pulsed ruby laser irradiation. It was found that such treatment caused the increase of crystal transmission in the absorption edge region and the rise of the free exciton band intensity with respect to that of its phonon replicas, while the luminescence related to deep centres did not show any changes. The changes in exciton luminescence and transmission spectra were accompanied with the increase of crystal conductivity. Comparison of obtained results with earlier data for CdS, CdTe, and ZnO crystals led to the conclusion that observed effect was due to interaction between dislocations decorated with mobile shallow donors and US wave excited by ruby laser pulse. High shallow donor density near dislocations results in formation of c-band state density tail and, therefore, in the shift of the absorption edge to the longwave side in these regions. Under US wave, the donors move from dislocations to the crystal bulk, the extent of dislocation decoration reduces, and the c-band state density tail shrinks, which led to the shrinkage of the absorption tail and to the rise of the shortwave wing of exciton luminescence. With time, mobile donors return to the dislocations, and the initial characteristics restore.

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