# DYNAMICS OF LASER-INDUCED DAMAGE OF ZnO SINGLE CRYSTAL

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**Abstract**

Monotonous increase of ZnO single crystal electrical conductivity up to 250 times was observed after irradiation by Nd:YAG laser. This effect is explained by increase of the Zn interstitial atoms' concentration at the irradiated surface of the crystal. At the same time, the improvement of ZnO crystal quality by laser intensity up to 3.2 MW/cm$^2$ takes place. The further increase of laser intensity led to emergence of cracks on the irradiated surface of the crystal and the dramatic decrease of the total photoluminescence intensity, especially, around the cracks. At the laser intensity 290 MW/cm$^2$ Zn nanoparticles were formed.

**Key words:** *ZnO crystal, Nd:YAG laser, Zn nanoparticles, damage, electrical conductivity*

The ZnO has been studied widely due to its unique electrical, optical, piezoelectric and magnetic properties [1]. Also, ZnO has potential applications in light emitting diodes, and near-UV or UV laser diodes [2, 3], transparent conductive thin films [1], solar cells [4].

Our previous investigations have shown the possibility to improve the ZnO single crystal quality using strongly absorbed Nd:YAG laser radiation [5]. However, at high laser intensity damage (ablation, fracture, cracking, etc) ZnO crystals were observed [6]. The aim of the present work is to determine damage thresholds of ZnO single crystal by studying the dynamics of laser-induced change of its electrical and optical properties.

The experiments were performed on hydrothermally grown n-type ZnO single crystals. It is known that hydrothermally grown ZnO contains Li atoms which substitutes Zn atoms forming a deep acceptor levels in bang gap of semiconductor that compensates n-type conductivity of ZnO caused by zinc interstitial atoms ($Zn_i$) and oxygen vacancies ($V_O$). The ZnO crystals were irradiated by the fourth harmonic of pulsed Nd:YAG laser Ekspla NL301G with following parameters: wavelength $\lambda = 266$ nm, pulse duration $\tau = 3$ ns and laser intensity up to $I_{max} = 300$ MW/cm$^2$. Photoluminescence measurements were performed using UV laser excitation by λ = 265 nm. Microstructural features of the samples were studied by scanning electron microscope (SEM). Topography measurements and electrical conductivity mapping were performed by atomic force microscope (AFM).

The typical photoluminescence (PL) spectra of ZnO consist of broad band at around 2.3 eV ascribed to deep-level emission (DLE) and the narrow band at hν = 3.3 eV ascribed to near band edge (NBE) emission [7], are shown in Fig.1. The DLE emission band could be related to $V_O$ and zinc vacancy ($V_{Zn}$) according to [8]. Usually, at room temperature the NBE emission is ascribed to free exciton. In Fig.1, the ZnO single crystal PL spectra of non-irradiated and irradiated by the laser intensity up to $I_{th1}$ = 3.2 MW/cm$^2$ are shown. In nonirradiated ZnO crystal DLE band is dominant band in PL spectrum. NBE band is asymmetric with shoulder in "red" part of spectra, as shown in Fig.1. At the same time, irradiation by the laser leads to dominance of the NBE emission band in PL spectrum, which became more asymmetric. The increase of free exciton band intensity and decrease of DLE band intensity usually is explained the improvement of crystal quality [8]. Moreover, deconvolution of excitonic band of non-irradiated ZnO crystal by Gaussian curves showed that it consists of at least two bands: a free exciton band (hν = 3.3eV) and at lower energy (hν = 3.1eV) – this band ascribed to Zn interstitial atoms ($Zn_i$) [9]. Irradiation by the laser at $I_{th1}$ = 3.2 MW/cm$^2$ leads to increase of $Zn_i$ band. At the same time, this threshold intensity causes increase of ZnO single crystal electrical conductivity by 5 times. It is known that, ZnO crystal has low energy of $Zn_i$ - $V_{Zn}$ pair formation in comparison to other native point defects, therefore, it is more likely that during irradiation $V_{Zn}$ and $Zn_i$ is formed. Therefore, the increase of electrical conductivity is explained by generation and concentration of $Zn_i$ atoms at the irradiated surface of the sample, due to temperature gradient field caused by strongly absorption of laser radiation - the so called thermogradient effect (TGE) [10]. The improvement of the crystal quality is explained by recombination of $V_{Zn}$ (defect, which appeared after crystal grow, initially) with $Zn_i$, which are concentrated at the irradiated surface of the sample, due to TGE. An evidence for this statement is decrease of DLE band and increase NBE band in PL spectra. The intensity of laser 3.2 MW/cm$^2$ is the first threshold which leads to ZnO crystal damage.

At higher laser intensity decrease of both DLE and exciton bands monotonously was observed, as shown in Fig.2. The second damage threshold was determined at $I_{th2}$=212.0 MW/cm$^2$. At this intensity extended defects, such as cracks are appeared. This effect is explained by mechanical compressive stress arising on the irradiated surface of the crystal due to non-homogeneous heating of the crystal by strongly absorption of the laser radiation.

At higher intensity ($I_{th3}$ = 250 MW/cm$^2$) $Zn_i$ combine into Zn nanoparticles, which explains the increase of electrical conductivity up to 250 times. This intensity leads to black ZnO formation, which was observed by naked eye.

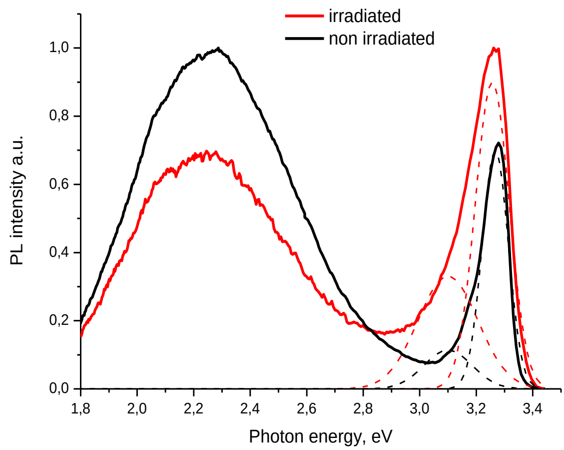


Fig.1. PL spectra of ZnO crystal before (black curve) and after (red curve) laser irradiation at $I_{th1}$=3.2MW/cm$^2$. Spectral resolution of spectrometr is 0.006 eV.

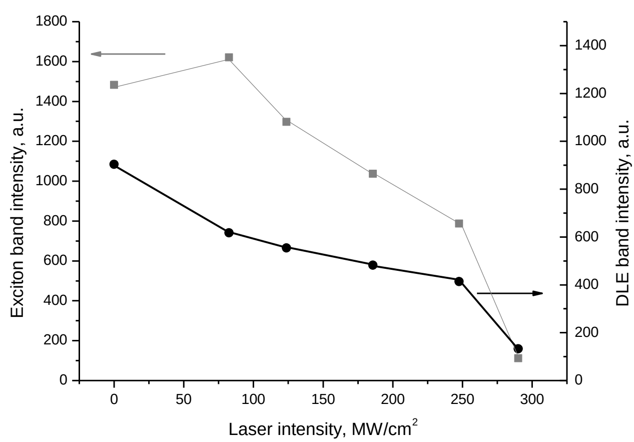


Fig.2. Exciton band and DLE band intensities as function of the laser intensity.

## Conclusions

1. The possibility to improve of ZnO crystal quality by the fourth harmonic of Nd:YAG laser radiation was shown.
2. Increase of conductivity up to 250 times is explained by generation and concentration of Zn interstitial atoms at the irradiated by Nd:YAG laser surface of ZnO crystal.
3. Formation of Zn nanoparticles with diameter up to 50 nm at the laser intensity 290 MW/cm$^2$ leads to black ZnO formation.

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