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# Origin of n-type conductivity in ZnO crystal and formation of Zn and ZnO nanoparticles by laser radiation

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## HIGHLIGHTS

- Zn interstitials as origin of n-type conductivity in ZnO crystal.
- Laser-induced thermal generation and redistribution of point defects.
- Controlled formation of Zn and ZnO nanoparticles by laser radiation.

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## ABSTRACT

Electrical and optical properties of hydrothermally grown ZnO crystal, as well as structural changes at its surface have been investigated before and after irradiation by pulsed Nd:YAG laser. The spreading resistance measurements have shown a monotonous increase of conductivity by three orders of magnitude when the laser intensity $I$ has been varied from zero to 290 MW/cm$^2$. The PL spectra have revealed an increase of concentration of Zn interstitials at the surface after irradiation by $I = 3.5$ MW/cm$^2$. Formation of Zn nanoparticles on the crystal surface has been observed at $I > 290$ MW/cm$^2$. The study of surface structure at $I = 315$ MW/cm$^2$ has shown that these Zn nanoparticles tend to transform into ZnO nanoparticles after an irradiation by more than 2 laser pulses. A theoretical model of thermal generation and redistribution of point defects has been elaborated to explain the origin of experimentally observed n-type conductivity. According to this model and experimental facts, the n-type conductivity originates from Zn interstitials, which are moved to the crystal surface by large temperature gradient during the laser processing. As a result, Zn-rich surface layer is formed and Zn nanoparticles grow, which are later oxidized into ZnO nanoparticles. We have shown a possibility to control the size distribution of these nanoparticles by choosing appropriate intensity and number of laser pulses.

## 1. Introduction

Metal oxides have been extensively investigated during last decades due to their special catalytic, anti-bacterial, as well as optical and electrical properties. Zinc oxide (ZnO), studied in our paper, is a metal oxide semiconductor. Because of its outstanding properties, such as high chemical stability, high electrochemical coupling constant, broad range of radiation absorption and high photostability, it is a multi-functional material [1,2]. Its applications range from tyres to ceramics, from pharmaceuticals to agriculture, and from paints to chemicals. In particular, ZnO, like several other metal oxides, has suitable photocatalytic properties [1–3] for applications in water splitting related to hydrogen energetic. For example, $TiO_2$, ZnO, $Co_3O_4$, $WO_3$, $F_3O_4$ and $MnO_2$ metal oxide nanosheets are used in photocatalytic systems for water splitting [4], whereas $TiO_2$, ZnO, $In_2O_3$, $Cu_2O$ and $WO_3$ are mentioned in [4] as appropriate 2D oxide photocatalysts. Heterostructured nanomaterials like $TiO_2$-$SnO_2$, ZnO-$TiO_2$, $TiO_2$-$V_2O_5$ [5], $TiO_2$-$WO_3$ [6], Ag-$Cu_2S$-PBO [7] as well as C-nanodots/$WO_3$ photocatalysts [8] are also used for many photocatalytic or light-triggered reactions. A review of photocatalytic and many other applications of ZnO is provided in [1,2,9]. The most commonly used catalysts are $TiO_2$ and ZnO. $TiO_2$ exhibits photoatalytic activity below the intensity of UV light. ZnO provides a similar or superior activity to that of $TiO_2$, but is less stable and less sensitive to photocorrosion [1]. However, better stability is provided by ZnO of nanometric dimensions, which offers better crystallinity and smaller defects. The photocatalytic activity of ZnO can be improved by adding other components.

Metal oxides are widely used in ceramic materials (e.g., ZnO, $BaTiO_3$) [1,10], in lithium-ion batteries as anode materials (e.g., $FeNb_{11}O_{29}$, $Li_4Ti_5O_{12}$, nano-$TiNb_2O_7$) [11,12], for catalytic reactions in

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chemical industries and petroleum refining (e.g., $\gamma$-$Al_2O_3$) [13,14], for oil-water separation (e.g., $TiO_2$) [15], as well as in thermoelectric power generation, solar cells, sensors, and other optoelectronic devices (e.g., $\alpha$-$Fe_2O_3$, $Na_xCoO_2$, $Ca_3Co_4O_9$, BiCuSeO, $CaMnO_3$, $SrTiO_3$, ZnO, $SnO_2$, $In_2O_3$) [1,2,16,17]. Metal oxides (e.g. $CoFe_2O_4$) along with other materials (e.g., carbon, $SiO_2$, polyaniline) are used composites and hybrid materials [18–21].

For a general review, some conductive materials and metamaterials [7,22–34] should be also mentioned with their applications such as polymer nanocomposites for sensing (e.g., polyurethane yarns for wearable sensing, thermoplastic polyurethane-graphene nanocomposites, graphene/thermoplastic polyurethane foams, electrically conductive thermoplastic elastomer nanocomposites, polylactic acid nanocomposites) [23,24,31,33,34], functional materials (e.g., polyimide nano-composites, metamaterials, graphene strengthened PVA nanocomposites, anti-adhesive cotton fabrics, carbon networks, carbon nanotubes) [7,22,27–30,32], energy harvesting (e.g., perovskite solar cells, dye-sensitized solar cells) [25,26], etc.

Apart from the diverse physical and chemical applications mentioned above, some metal oxides like ZnO and $TiO_2$ are extensively used in medicine owing to their anti-bacterial properties [9].

In our paper we focus on the electrical and optical properties of ZnO. These properties of ZnO make it suitable for potential applications in optoelectronic devices [35], such as: LED, UV laser diodes, and solar cells. ZnO crystal can be both highly transparent and highly conductive material, therefore, it is an appropriate candidate for the best transparent conducting oxide.

Atoms of metal, such as Al, Ga, and In, are widely used as n-type impurities in ZnO crystal to provide its high conductivity [36]. However, at high concentration of such doping, formation of metallic inclusions takes place, which leads to the decrease of conductivity of the crystal and its deformation [37]. Moreover, up today metal nanoparticles are widely used in solar cell technology to increase efficiency [38], using the surface plasmon resonance [39]. Another approach has been proposed in [40], allowing to increase ZnO conductivity using intrinsic defects, for example, Zn interstitials ($Zn_i$).

The origin of n-type conductivity has been studied during many years. It has been proposed earlier [41] that oxygen vacancies play the major role in the n-type conductivity of pure ZnO crystal. The possibility to modify electrical properties of polycrystalline ZnO by a continuous wave Yb fiber laser irradiation with wavelength $\lambda = 1070$ nm has been shown [42]. A sharp drop of resistivity of ZnO layer has been observed after the laser irradiation, explaining this by the formation of oxygen defects through the thermal process in accordance with the above mentioned conception that oxygen defects play the major role in conductivity.

However it was soon established, that n-type conductivity in pure ZnO crystal is basically provided by $Zn_i$ [43,44]. According to the defect formation energies evaluated in [45], oxygen vacancies ($V_O$) are the dominant native point defects in this case. The general belief, supported by the density functional calculations, e.g., in [45], is that $V_O$ are deep donors, which are neutral in normal state and, therefore, cannot essentially contribute to the conductivity at room temperature.

Nevertheless, the charge state of $V_O$ remains a controversial issue. Recently, it has been argued [46] that $V_O$ is $+2$ charged rather than neutral. According to the $V_O$ formation energy depending on the Fermi level $E_F$, shown in Fig. 2 of [45], the normal state of this defect in Zn-rich ZnO is indeed $+2$ charged for $E_F < 2$ eV. It explains the discussed in [46] fact that the Zn-rich ZnO usually has *n*-type conductivity, since$E_F < 2$ eV must hold for the *p*-type conductivity (the Fermi level should be close enough to the valence band maximum). Namely, impurity acceptors are compensated by oxygen vacancies as donors when one tries to move the Fermi level below 2 eV by doping. It has been argued in [46] that $V_O$ is $+2$ charged even close to the conduction band minimum (CBM). However, only an indirect evidence has been provided there, which is based on measurements of the diffusion activation energy of $V_O$, making assumptions about that how this energy is related to the $V_O$ charge state and electron Fermi level. It has been found in [46] that this activation energy depends on the Fermi level, concluding from this fact that $V_O$ is charged. However, a different interpretation is possible. For example, a diffusion jump can occur through an intermediate state, which contains a point defect like a complex of double oxygen vacancy and an interstitial oxygen atom. This complex might be charged. In this case, the diffusion activation energy is $E_F$ – dependent if a single oxygen vacancy is neutral. It is because the formation enthalpy of a charged point defect linearly depends on $E_F$ [45,46]. Our experimental data of conductivity can be reasonably explained based on the general belief that oxygen vacancies are deep donors, i.e., neutral in normal state near CBM. Therefore we follow this conception.

Since laser processing is very time-efficient and friendly to surrounding environment, the effect of powerful laser radiation on the electrical and optical properties of ZnO crystal has been widely studied [47–49]. The change of optical properties, such as photoluminescence (PL) and absorption spectra [50], and electrical characteristics [43]: resistivity, electron and hole mobility of undoped ZnO crystal after irradiation by ruby laser was investigated. Such laser radiation, the so-called two-quantum excitation, leads to the homogeneous excitation of the crystal volume. It was shown that, after irradiation by the laser at intensity in the range of $I = 200–400\ \mathrm{MW/cm^2}$, crystal became optically more transparent, the intensity of exciton band in PL spectrum increased and, at the same time, the electric conductivity grew too. This phenomenon is explained by the increase of $Zn_i$ concentration due to the formation and propagation of ultra-sonic waves in the crystal, which are formed by laser pulses. Our previous investigations have shown the possibility to improve the quality of ZnO single crystal by strongly absorbed pulsed Nd:YAG laser radiation [40] due to the increase of $Zn_i$ concentration at the irradiated surface. Recently, the formation of "black ZnO" after irradiation of the crystal by UV eximer laser was discovered [51]. An explanation of this phenomenon has been proposed in [51], according to which Zn nanoparticles emerge on the irradiated surface of ZnO crystal due to the evaporation of oxygen atoms. Another explanation has been provided in [40], according to which the formation of Zn nanoparticles takes place due to drift of Zn interstitials towards the crystal surface in nonhomogeneous temperature field during the pulsed laser irradiation.

Thus, here we address an important question about the mechanism of laser-induced phase transitions. The formation of Zn nanoparticles by pulsed laser radiation and the following transformation of them into ZnO nanoparticles are the examples of laser-induced phase transitions considered in our work. These transitions are quasi-adiabatic, since the heat diffusion is small during a nanosecond laser pulse. At the same time a very large temperature gradient arises. It makes a great difference between the laser-induced quasi-adiabatic phase transitions and isobaric phase transitions in furnace. In particular, we show that the laser-induced motion of atoms, caused by the temperature gradient, results in the formation of Zn nanostructures in solid phase even without any melting.

Moreover, the laser treatment reveals a possibility to form Zn and ZnO nanoparticles of controlled size distribution [40]. Here we analyse this distribution, using its three-dimensional representation. The formation of nanoparticles of the desired size by laser radiation is a step towards new laser technology in optoelectronics and microelectronics.

Recently, we have shown the possibility to increase the conductivity and to form Zn nanoparticles in hydrothermal ZnO crystal by Nd:YAG laser radiation using intrinsic defects of the crystal – Zn interstitials [40]. For this aim we have used the strongly absorbed fourth harmonic of Nd:YAG laser radiation ($h\nu > E_g$, where $h\nu$ – photons energy of laser and $E_g$ – the band gap of ZnO).

In the current study, we propose a theoretical microscopic model for calculation of concentration of point defects. The aim of this work is to give an explanation of the conductivity measured in ZnO crystal, depending on the intensity of pulsed Nd:YAG laser radiation, based on