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Annealing Effect on the Structural, Electrical and Optical Properties of Er, Li-Codoped ZnO Films

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The effect of post deposition annealing in air on structural, electrical and optical properties of Er,Li-codoped ZnO films deposited on sapphire substrate by an e-beam evaporation technique in vacuum are investigated. The structural, optical and electrical features of these films before and after short-time annealing were studied by XRD, UV-VIS-IR absorption and reflection spectroscopy, photoluminescence and resistivity measurements. Experimental results showed that there is wide absorption band in IR range, connected with defect centers, presumably OH-complex, in as-deposited films, and after annealing it is disappeared. Green and NIR photoluminescence of Er^{3+} ions in annealed films excited under nitrogen laser was observed. The intensity of photoluminescence is much stronger for sample with Li (0.8 %) than that with Li (0.6 %).

Keywords: ZnO Films, Er^{3+} Photoluminescence, Optical Properties.

PACS numbers: 78.30.Fs, 78.55.Et

1. INTRODUCTION

RE–doped wide gap semiconductors have attracted considerable interest in recent years as a basis for optoelectronic devices, which combine the electronic properties of semiconductors with unique luminescence features of RE ions. Among all semiconductors, ZnO is considered to be a promising candidate as host material for Er doping due to the fact that ZnO satisfies two important requirements, oxygen codoping and wide-band-gap materials (band gap of ~3.3 eV) with higher exciton binding energy (60 meV). On the other hand, Er-doped ZnO is an important material for light-emitting diodes, laser diodes, and optical amplifiers operating at ~ 1.54 μm in the waveguide structure due to their high transparency and low electrical resistivity (up to ~ $6.41 \cdot 10^{-4}$ Ω cm) [1, 2]. The Li^{+} ion is metallic ion with smallest cationic radius, and is favorable for its movement and localization in the host lattice. It is possible that Li^{+} ions occupy the interstitial sites between Er^{3+} and Zn^{2+} ions in the pseudo-octahedral structure [3]. The enhancement of the PL intensity at ~ 1.54 μm in the Li- and Er-codoped ZnO nanocrystals [4] and films, prepared by pulsed laser deposition on Si substrate [3], has been reported.

The purpose of the present work was to obtain Li, Er-codoped ZnO films by vacuum electron-beam evaporation from polycrystalline targets and to study structural, electrical and optical properties of the obtained films before and after short-time annealing in air. Special attention was focused on investigations of photoluminescence (PL) of Er^{3+} ions in the visible and NIR ranges of spectrum under nitrogen laser excitation by 337.1 nm radiation.

2. CONDITIONS OF EXPERIMENTS

The Li, Er-codoped zinc oxide films were prepared by vacuum electron-beam evaporation technique on sapphire substrates. The synthesized ceramic pellets of Li, Er-codoped zinc oxide were used as targets for deposition. For fabrication of targets ZnO powders with the purity of 99.98 % were used. The impurities were doped as Er_2O_3 and $LiOH{\cdot}H_2O$. The annealing of pellet was performed in air at 1430 °C / 1 h. Duration of temperature rise and decay were 18 *h* and 10 *h* respectively. The films were prepared under following conditions: the energy of electrons was about 6 keV, the substrate temperature was maintained at 250°C. The film growth rate, depending on electron-beam energy, substrate temperature and vacuum value, was 2 Å/s. The distance between the target and the substrate was maintained constant and amounted to 19 cm. Short-time annealing in air at 600 °*C* / 7 min for ZnO:Er (1 %), Li (0.8 %) film and at 660 °*C* / 8 min for ZnO:Er (1 %), Li (0.6 %) film were performed. Choice of such lithium impurity content was associated with our previous work [5], in which there was a sharp change in the physical properties of the films at these concentrations of lithium. Crystal quality and orientation of obtained films was established by the X-ray diffraction (XRD) method with the help diffractometer using the emission of CuKα ($\lambda = 0.1542$ nm). The transmission and reflection spectra were recorded at room temperature with the use of UV, visible, and IR spectrophotometers. The pulse-type nitrogen laser LGI-21 with pulse duration 7 *ns*, pulse repetition frequency of 100 Hz, average power of 3 mW and the wavelength $\lambda = 337.1$ nm is used as a source of excitation of PL. The energy density per pulse at a defocused beam is 10 kW/cm². The PL spectra at 77 K were recorded by means of synchronous-phase amplifier and spec-

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trometer MDR-23 with InGaAs-photodetector in IR and with photomultiplier FEU-79 in the visible range. Recording of signal and control of monochromator was realized with experimental scheme shown in [6].The erbium concentration in films was determined by an electron scanning microscope with the system of microanalysis based on the excitation of characteristic XRD. The thickness of films determined interferometrically from reflection spectra R and studied film had a thickness d = 700 nm for ZnO:Er (1 %), Li (0.6 %) and d = 900 nm ZnO:Er(1 %), Li(0.8 %). The electrical resistivity of films was measured by the four-probe technique.

3. DISCUSSION OF RESULTS

Only (0002) peak appears in the XRD pattern of Li, Er-codoped ZnO film (Fig. 1) suggesting that the film is of hexagonal wurtzite structure with preferred c-axis orientation. This shows absence of any phases related to Er or Li in the film. It is also found that the full width at half maximum (FWHM) of the (0002) peak decreases from 0.5° to 0.3° as a result of annealing. It could be attributed to an improvement in the crystallized quality after annealing.

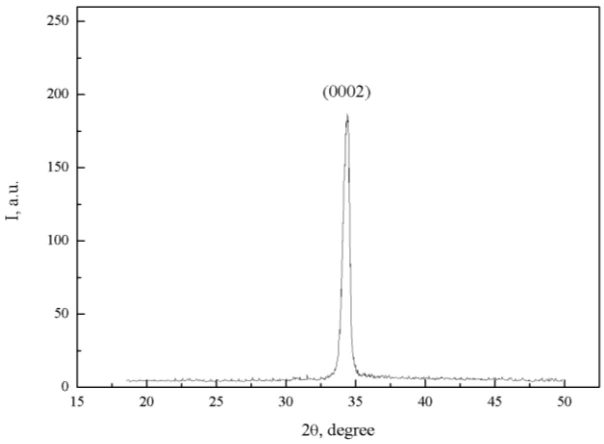

Fig. 1 – XRD spectrum of Er, Li-doped ZnO films on sapphire substrate

Optical transmission spectra T of obtained films measured in the spectral range 300–5000 nm at room temperature revealed a high degree of transparency of the films ($T \approx 85$ % in the visible range) and an abrupt UV edge of absorption. Transmission spectra of Er, Li-doped ZnO films on sapphire substrates before and after annealing in air in UV and IR ranges are shown in Fig. 2a and Fig. 2b, accordingly. Beside the interference fringes arising at reflection from boundaries of a film-substrate and a film-air, the wide absorption band from 1000 to 6000 cm^{-1} in IR range of a spectrum, are seen. Work [7] connects the absorption band near 3400 cm^{-1} with vibrations of OH-complex. OH groups with high vibration frequency can increase the non-radiative relaxation rate and hence decrease efficiency of PL. It indicated that the enhancement of PL intensity may also be caused by the reducing number of OH groups. It is possible that the target is not fully dense and contains pores, wherein the trapped moisture and the additional elements (hydrogen and oxygen), may reside.

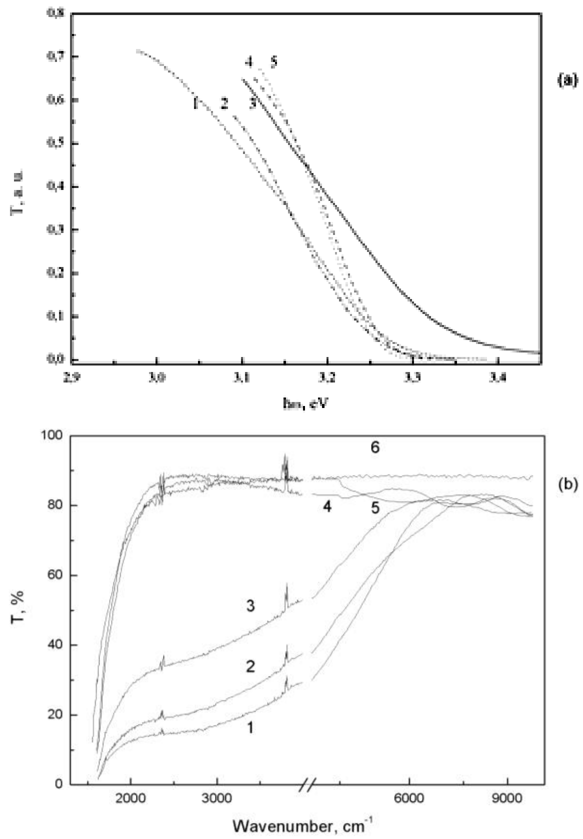

Fig. 2 – Transmission spectra in UV (a) and IR (b) ranges of ZnO:Er (1 %),Li (0.8 %) (1 and 3) and ZnO:Er (1 %),Li (0.6 %) (2) films before annealing and the same after annealing in air, respectively (4 and 5), and (6) is sapphire substrate

UV edge of transmission T and determined from it absorption coefficients α of obtained films for determination of the band gap E_g were used. This value was obtained by extrapolation of the linear part of the dependence of $(\alpha h\omega)^2$ on the photon energy $h\omega$ to intersection with the energy axis (at $\alpha = 0$) with the assumption of direct transitions from the valence band to the conduction band. Determination of E_g value is illustrated in Fig. 3 and it amounts 3.27 eV and 3.28 eV for the as-deposited ZnO:Er (1 %), Li (0.8 %) and ZnO:Er (1 %), Li (0.6 %) films respectively, and after annealing in air this value decreases to 3.26 eV for both films. As a result of annealing energy band gap of Er, Li- doped ZnO films becomes narrower.

This is consistent with the results of electrical resistivity measurements. The electrical resistivity of ZnO:Er (1 %), Li (0.8 %) and ZnO:Er (1 %), Li (0.6 %) films increases from ~ $2 \cdot 10^{-2}$ Ωcm for as-deposited films up to ~ 10^{6} Ωcm for annealed films. The resistivity increase by the heat treatment is mainly due to the decrease in carrier concentration.

PL at 77 K of as-deposited and annealed Er, Li-doped ZnO films under exciting radiation from nitrogen laser at 337.1 nm was studied in UV, visible and NIR ranges. A nitrogen laser at 337.1 nm was used as the above-band-gap excitation source, but typical near-band edge emission band at ~380 nm is absent in all the studied films.

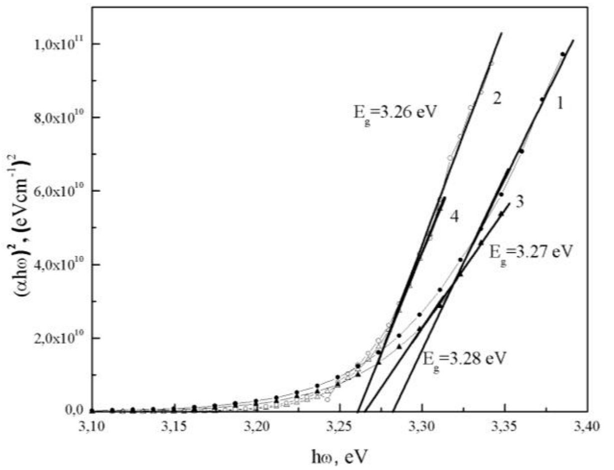

Fig. 3 – Dependence of $(\alpha h\omega)^2$ on the photon energy $h\omega$ for determination of the band gap E_g of ZnO:Er (1 %), Li (0.6 %) (1 and 2) and ZnO:Er (1 %), Li (0.8 %) (3 and 4) films on sapphire substrate before annealing (1 and 3) and after annealing in air (2)

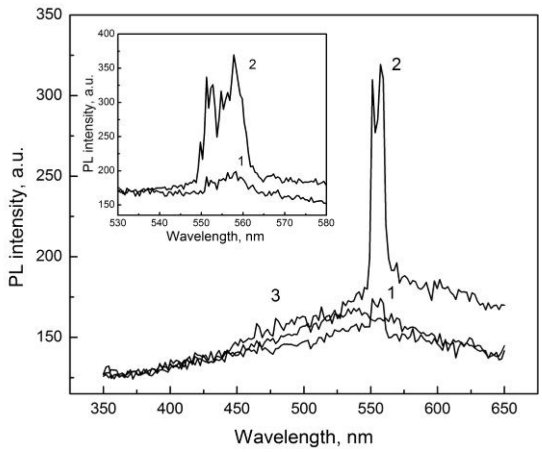

Fig. 4 – PL spectra in visible range for ZnO:Er (1 %), Li (0.6 %) (1) and ZnO:Er (1 %), Li (0.8 %) (2) films on sapphire substrate after annealing in air with Er^{3+} emission on ${}^4S_{3/2}$, ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition and (3) is an emission from excitation laser and cryostat

PL at 77 K of as-deposited and annealed Er, Li-doped ZnO films under exciting radiation from nitrogen laser at 337.1 nm was studied in UV, visible and NIR ranges. A nitrogen laser at 337.1 nm was used as the above-band-gap excitation source, but typical near-band edge emission band at ~ 380 nm is absent in all the studied films. For as-deposited samples the Er^{3+} emission of Er^{3+} ion is absent and very weak for annealed ZnO:Er (1 %), Li (0.6 %) film, but significantly enhanced for ZnO:Er (1 %), Li (0.8 %) one. Fig. 4 shows PL spectra of Er, Li-doped ZnO films obtained at 77 K in visible range. The green emissions are assigned to the transitions of ${}^4S_{3/2}$, ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions as in [8, 9]. The spectra in Fig. 5 correspond to the transition from the first excited state ${}^4I_{13/2}$ to the ground state ${}^4I_{15/2}$ and are characterized by the principal peak at ~ 1.54 μm. The shape of obtained spectra is similar to the data [3, 4]. The intensity of green emission is much stronger for sample with Li (0.8 %) than that with Li (0.6 %) and NIR emission band did not recorder from sample with Li (0.6 %).

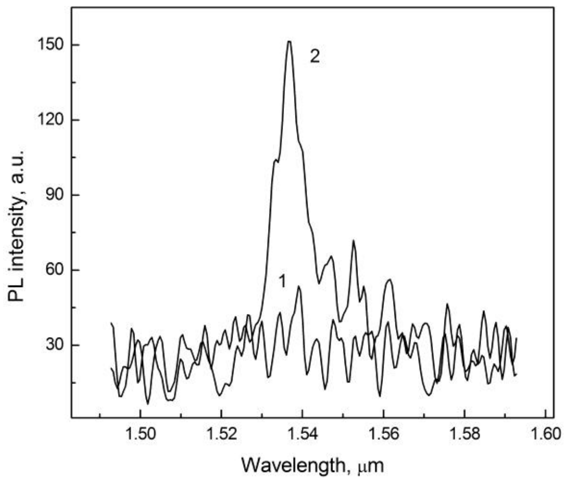

Fig. 5 – PL spectra in IR range for ZnO:Er (1 %),Li (0.6 %) (1) and ZnO:Er (1 %), Li (0.8 %) (2) films on sapphire substrate after annealing in air

4. CONCLUSION

Thus, Li, Er-codoped zinc oxide films with a high degree of transparency (~85 %) in the visible and IR range have been obtained by electron-beam evaporation technique in vacuum. Both the as-grown and post-annealed films exhibit good crystalline quality with preferred c-axis orientation. Transmission spectra of as-deposited Er, Li-doped ZnO films contain a wide absorption band in IR range, connected perhaps with OH-complex. Short-time annealing in air of these films leads to the disappearance of this band. After post-annealing treatment of Er, Li-doped ZnO films green and near 1.54 μm PL emission related to intra-4*f* shell of Er^{3+} ions are observed.

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