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Transformations in the photoluminescent, electrical and structural properties of Tb^{3+} and Eu^{3+} co-doped ZnO films under high-temperature annealing



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ABSTRACT

The effect of thermal annealing on optical, electrical and structural properties of Tb and Eu co-doped ZnO films grown by magnetron sputtering on Si and Al_2O_3 substrates was investigated by X-ray diffraction, photoluminescence, micro-Raman and IR reflection methods. It is shown that incorporation of rare earth ions in ZnO is accompanied by the formation of intrinsic defects. The as-deposited and annealed at 600 °C films demonstrate Tb^{3+} emission and no Eu^{3+} one. Higher intensity of Tb^{3+} photoluminescence in the films on Al_2O_3 substrate as compared with that on Si is ascribed to higher content of Tb^{3+} emitting centers. The model of these centers including the substitutional Tb and interstitial oxygen is proposed. In the excitation spectra of Tb^{3+} emission no for crystalline terbium oxide and silicate phases. In the photoluminescence spectra, the decrease of Tb^{3+} emission and the appearance of two sets of Eu^{3+} related bands caused by energy transfer from Tb^{3+} to Eu^{3+} ions are found. This is ascribed to segregation of rare earth ions in the additional phases and the decrease of the distance between the ions.

1. Introduction

Zinc oxide (ZnO) is a promising material for semiconductor device applications due to its unique electrical, optical and piezoelectric properties [1, 2, 3]. Rare earth (RE)-doped ZnO exhibiting emission of specific color is receiving great attention for potential applications in light emitting diodes (LEDs), plasma displays and fluorescent lamps [4, 5, 6, 7]. In particular, incorporation of Tb^{3+} ions into ZnO host allows producing the sources of green emission [4,5], while Eu³⁺ ions in ZnO are used for obtaining the red one [6,7]. The specific emission of Tb and Eu ions embedded into ZnO can be obtained by using both resonant excitation of RE ions and the near-UV excitation. The latter is usually ascribed to light absorption in ZnO followed by energy transfer from the host to RE ions. However, different conclusions on the efficiency of photoluminescence (PL) of RE ions under such indirect excitation as well as on the mechanisms of energy transfer from ZnO to RE ions were considered. Usually [8, 9, 10], resonant photoexcitation of RE ions results in larger PL intensities than excitation of the ZnO host. At the same time, in [11, 12] an indirect excitation of Eu-related emission was found to be more efficient than the direct one. It was assumed that one of the reasons of low efficiency of energy transfer from ZnO host to RE ions is the short lifetime of exciton in ZnO and/or non-radiative energy dissipation that depends on host crystallinity [13]. On the other hand, the enhancement of the intensity of RE ion luminescence under non-resonant excitation was supposed to be due to defect-mediated energy transfer from ZnO to RE ions.

Several models of the energy transfer from ZnO host to RE ions were proposed. One of them supposes the defect-mediated process including levels of intrinsic radiative defects [14, 15, 16]. The second one assumes that the electron hole pairs produced by the above bandgap excitation of ZnO form free excitons which then recombine through the UV near-band-edge emission or transfer their energy to RE ions [17]. In another model, the generated free carriers are trapped by RE-related impurity state and form a bound exciton which, when recombined, excites 4f core levels through resonant or non-resonant Auger scattering [17, 18].

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Fig. 1. XRD patterns of the as-deposited (AD) and annealed films of Tb, Eu co-doped ZnO on Si (a) and Al_2O_3 (b) substrates. The spectra are shifted in vertical direction for clarity. The intensities are given in logarithmic scale.

A clear evidence of the energy transfer from ZnO host to RE ions could be the presence in the PL excitation spectra (PLE) of RE ion of a peak at about 370–380 nm corresponding to the free exciton absorption in ZnO. However, different PL excitation spectra are given in different works. In some cases, the excitation spectra showed this maximum [14,17], while in other ones such a feature was not observed [19]. It should be noted that in some reports [14,19] the peak corresponding to band-to-band (exciton) transition in the PL excitation spectra was observed when the defect-related band of ZnO overlapped with the emission of RE ions of comparable intensity. In this case, the peak can correspond to excitation of defect-related band. It should be noted also that in the case of Eu³⁺-related emission, its resonant excitation via ${}^{7}F_{0}{}^{-5}L_{6}$ transition overlaps with exciton absorption. Thus, the energy transfer from ZnO to RE³⁺ ions remains questionable.

To enhance the emission of specific RE ion, the co-doping with another RE ion that can transfer excitation energy is used. The codoping is also a strategy for producing multicolor emission appropriate for achieving white light.

In general, the energy transfer among RE ions in solids occurs nonradiatively via the electric dipole-dipole or electric dipole-quadrupole interactions [20]. Specifically, it has been shown that Eu^{3+} emission in ZnO can be increased by co-doping with Tb owing to efficient resonant energy transfer from Tb³⁺ to Eu^{3+} [19, 20, 21, 22].

Another important factor influencing the efficiency of luminescence of trivalent RE ions in ZnO is a large difference in the ionic radius and in the charge state of the RE and Zn^{2+} ions that causes a difficult RE ion incorporation into ZnO matrix. The excess charge can be compensated by intrinsic defects or impurities. Specifically, the co-doping with Li ions had been proposed to increase the solubility of trivalent RE ions in ZnO host [7, 12, 23, 24]. In turn, lattice strain caused by incorporation of RE ions can result in their segregation and formation of other oxide phases more particularly upon anneal treatments.

The intensity of RE ion luminescence in ZnO thin films can also depend on the substrate nature [11, 13, 25]. Specifically, the intensity of Tb-related luminescence was found to be higher in the film on Al_2O_3 or SiO₂ substrates as compared with the film on Si [25]. It was supposed that non-radiative energy dissipation on defects that depends on crystallinity of the film is the main factor characterizing the dependence of emission intensity on substrate type [11,13]. Alternatively, the observed difference in the PL intensity of RE ions was assumed to be caused by the difference in the density of points defects that enhance the energy transfer from ZnO [11]. However, the different content of emission centers as the reason of the difference in PL intensity was also considered [25].

In this work, we focus on a study of the excitation mechanisms of Tb and Eu-related emission, structure of emitting RE-related complexes as well as on the effect of substrate material on RE-related luminescence and film conductivity of (Tb,Eu) co-doped ZnO films deposited on silicon and sapphire substrates by RF magnetron sputtering.

2. Experimental details

The films doped with Tb (3 at%) and Eu (lower than 0.3 at%) were deposited on Si (100) and c-cut Al_2O_3 substrates in one run. A bottomup RF magnetron sputtering of ZnO target topped simultaneously with Tb_4O_7 and Eu₂O₃ calibrated pellets was performed in an argon plasma. The substrates' temperature was 100 °C. More details about deposition procedure can be found elsewhere [26, 27]. The thicknesses of the films grown on Si and Al_2O_3 substrates were obtained by ellipsometry method and found to be about 840 and 680 nm, respectively. The films were post annealed at 600 and 900 °C in nitrogen flow during 1 h.

The structural, luminescence and electrical properties of the films were studied by X-ray diffraction (XRD), micro-Raman, PL, PL excitation (PLE) and IR reflection methods. The XRD data were collected using X-ray diffractometer Philips X'Pert-MRD with the Cu Ka₁ radiation ($\lambda = 0.15418$ nm). The patterns were recorded in the Bragg-Brentano (Θ -2 Θ) geometry. The micro-Raman and micro-PL spectra were measured in a quasi-backscattering geometry using a triple Raman spectrometer Horiba Jobin-Yvon T64000 integrated with Olympus BX-41 microscope and air-cooled CCD detector. As excitation source, a 488.0 nm line of an Ar-Kr laser and a 325 nm line of He-Cd laser were used. The PL and PLE spectra were recorded using a spectrofluorometer FluoroLog-3 setup. The IR reflection spectra were measured using a Bruker Vertex 70 V FTIR spectrometer equipped with a Globar source and a deuterated triglycine sulfate (DLaTGS) detector with polyethylene window. The spectral resolution and incidence angle was 1 cm^{-1} and 13° , respectively. The IR spectrum of a gold mirror was used as a reference.

3. Results and discussion

3.1. XRD study

The XRD patterns of the as-deposited (AD) films on Si and Al_2O_3 substrates (Fig. 1(a) and (b), respectively) contain the peaks at $2\Theta \sim 31.8^\circ$, $\sim 34^\circ$ and $\sim 72^\circ$ caused by reflections from (100), (002) and (004) planes of hexagonal ZnO, respectively [28]. As expected, the highest intensity of the peak at $\sim 34^\circ$ testifies to the predominant

growth orientation of ZnO grains along the c-axis.

The (002) peak position is shifted to lower angles compared to the (002) peak of relaxed bulk ZnO (34.44°) and is found at 33.4° and 34.26° for the films on Al_2O_3 and Si substrates, respectively. This testifies to the presence of tensile stress along *c*-axis, being the most pronounced in the case of oxide substrate. The coherent domain size *d*, estimated from XRD data using Scherrer formula, was found to be ~34 nm for the as-deposited films on both type of substrates.

The annealing results in the shift of (002) peak position to higher angles showing tensile stress relaxation. At the same time, the coherent domain size does not change significantly. Besides, additional peaks at 21.8 and 28.7° appear in the XRD patterns of the films annealed at 900 °C (Fig. 1). The first peak is observed for the film on Si substrate only and coincides with reflection from (300) planes of Zn_2SiO_4 . The second one is found for both films and its position is close to (222) reflection of Tb_2O_3 as well as to (111) reflection of TbO_2 . These results show that whatever the substrate type, the conventional thermal annealing at 900 °C of Tb, Eu co-doped ZnO films stimulates out-diffusion of RE ions from ZnO grains and segregation with subsequent formation of crystalline terbium oxide phase.

3.2. Raman scattering study

The non-resonance micro-Raman spectra of ZnO films grown on Al_2O_3 and Si substrates demonstrate E_2^{low} , E_2^{high} and $qA(E)_1(LO)$ phonon modes that are overlapped with the signals from the corresponding substrates (Fig. 2). In the spectra of as-deposited films, the E_2^{high} peak has low intensity and is shifted to the low energy side as compared to the peak position in relaxed undoped ZnO ($\omega_0 = 437,0$ cm⁻¹). The E₂^{high} mode is associated with oxygen-atom vibrations and its frequency is highly sensitive to applied stress. The low energy shift of the E2^{high} peak testifies to the presence of biaxial tensile stress in the plane of substrate that can be induced by the: (i) lattice mismatch between the ZnO film and the Si substrate; ii) both the impurity atoms and intrinsic defects formed due to doping. The weak intensity and large FWHM of E_2^{high} phonon band suggest low crystal quality and high level of structural defects. The appearance of qA(E)₁(LO) mode at 581.8 cm⁻¹ also testifies to the formation of intrinsic defects in the oxygen sub-lattice of ZnO [29, 30]. Generally, the $A_1{}^{\rm LO}$ mode is weak because of two opposing contributions from the Frohlich interaction and the deformation potential [31]. However, the breakdown of translational symmetry due to structural disorder caused by a random incorporation of the dopant will lead to alloy potential fluctuations. As a result, the spatial correlation function of the phonon becomes finite and phonons with large q vectors can participate in Raman scattering, resulting in an enhancement and broadening of the A₁^{LO} mode [32]. Doping of ZnO changes the ratio of these contributions resulting in the

increase of qA(E)1(LO) mode intensity.

Note also, that the peak position of E_2^{low} mode caused by zinc-atom vibrations is shifted to lower frequencies as compared to the corresponding peak position in relaxed undoped ZnO ($\omega = 101 \text{ cm}^{-1}$) [33]. This argues to RE ion incorporation onto Zn^{2+} site as substitutional atom. The tensile stress, the shift of E_2^{low} mode and prominent qA(E)₁(LO) peak caused by defect formation are the evidence of RE ion incorporation into ZnO. It agrees with the results of other authors showing that RE doping creates disorder and stimulates intrinsic defect formation in ZnO lattice [34, 35].

The Raman spectra of the annealed films show the decrease of $qA(E)_1(LO)$ mode intensity indicating the decrease of intrinsic defect content (Fig. 2). Besides, the E_2^{high} mode increases in intensity and shifts to high energy side, which is in favor of the improvement of crystal structure and relaxation of stress under annealing. These changes in Raman spectra can be ascribed to impurity segregation.

3.3. PL and PLE study

The PL spectra of the AD films excited with a 325 nm light show the ZnO exciton band (peaked at ~380 nm) and defect related one, as well as the Tb³⁺-related PL bands centered at 490, 545 and 586 nm corresponding to 4*f* transitions. However, Eu³⁺-related emission is not detected most probably due to low Eu content (Fig. 3). The intensity of ZnO exciton and defect-related PL is higher in the film on Si substrate. At the same time, Tb-related emission is more efficient in the film grown on Al₂O₃ that is consistent with the higher intensity of $qA(E)_1(LO)$ mode. Therefore, it can be concluded that the formation of optically active Tb³⁺-related centers is accompanied by the formation of intrinsic defects in oxygen sub-lattice.

The annealing changes the exciton band intensities of both films in different ways. For the films deposited on Si substrate, a monotonic decrease of the exciton PL intensity is observed, while the films grown on Al_2O_3 demonstrate an intensity increase after annealing at 600 °C and a decrease after annealing at 900 °C. The intensity of defect-related PL band also changes in different ways in the films on different substrates. In the films on Si substrate, it decreases after annealing at 600 °C and increases after annealing at 900 °C, while in the films grown on Al_2O_3 , it evolves only slightly. The non-monotonic behavior of the intensity of exciton and defect-related PL of ZnO can be caused by the variation of the number of the centers of radiative and non-radiative recombination. The latter, in particular, can be caused by the improvement of crystalline structure due to impurity segregation.

An annealing results in the decrease of the intensity of Tb-related emission for both types of films. For the film on Al_2O_3 substrate, this effect is more appreciable. This behavior of Tb^{3+} PL emission can be ascribed to Tb segregation, which is in agreement with Raman



Fig. 2. Micro-Raman spectra of as-deposited and annealed at 600 and 900 °C (Tb, Eu)-ZnO films deposited on Si (a) and Al_2O_3 (b) substrates. The Raman spectra of corresponding substrates are also shown and the phonon modes of Al_2O_3 and Si substrates are labeled as "S" and "Si" respectively; $E_{exc} = 2.54 \text{ eV}$.



Fig. 3. PL (solid lines) and PLE (dashed lines) spectra of as-deposited (AD), 600 °C and 900 °C annealed films grown on Si (a) and Al_2O_3 (b) substrates. PL spectra were excited with 325 nm light, PLE spectra were detected at 545 nm. Red arrows show the Eu³⁺ PL transition ${}^{5}D_{0}{}^{-7}F_{2}$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. The dependence of the intensity of Tb³⁺ PL band (peaked at 545 nm) measured under 325 nm light excitation (a) and qA(E)₁(LO) Raman mode (b).

scattering data showing the decrease of $qA(E)_1(LO)$ Raman mode intensity in the annealed films (Fig. 4).

As it was mentioned above, the intensity of Tb-related emission of AD films depends on the substrate nature. Figs. 3 and 4 show that the dependencies of PL band and $qA(E)_1(LO)$ mode intensity versus the annealing temperature are also different for the two substrates. This can be caused by a redistribution of recombination flow between the different recombination channels, including recombination through exciton, non-radiative and radiative intrinsic defects and impurities.

To elucidate the reason of higher Tb^{3+} PL intensity in the film on Al_2O_3 substrate, the spectra of both types of films annealed at 600 °C were analyzed. As Fig. 3 shows, the intensities of exciton and defect-related bands are higher in the film on Al_2O_3 substrate, but the intensity of Tb-related emission is also higher. Therefore, more efficient Tb^{3+} PL in this film cannot be explained by the lower content of non-radiative or radiative intrinsic defects. Thus, we can suppose that the higher intensity of Tb-related emission in the film grown on Al_2O_3 substrate is due to higher number of optically active Tb^{3+} centers in this film.

The analysis of the PL spectra of the films annealed at 900°C revealed another peak at 611 nm (Fig. 5, a). This spectral position agrees with ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ ions. This PL band is also well observed in the spectra measured under 275 nm light excitation corresponding to $4f^{7}5 d^{1} \rightarrow {}^{7}D_{i}$ transition of Tb³⁺ ions (Fig. 5 b,c).

The PLE spectra of Tb-related luminescence in the AD and 600 °C annealed films demonstrate a shoulder at ~300 nm (Fig. 3) which can be ascribed to $4f^{7}5 d^{1} \rightarrow {}^{9}D_{J}$ transitions of Tb³⁺ ions [36]. At the same time, the features connected with light absorption in ZnO host were not observed. However, in the PLE spectra of the films annealed at 900 °C

(Fig. 3), the additional maximum at about 370 nm is found and it can be ascribed to exciton absorption in ZnO. This maximum appears when Tb-related emission decreases and become comparable or lower in intensity than the defect-related band. Therefore, it could be apparently connected with excitation of defects related band. In fact, this feature is more pronounced in the PLE spectrum of the film on Si substrate (Fig. 3,a) where the intensity of defect-related band is higher.

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This allows supposing that Tb^{3+} ions are not excited through energy transfer from ZnO host when 325 nm light is used. On the other hand, the PLE spectra taken at 545 nm give the evidence on the large broadening of RE-related absorption band that can be caused by local crystal field surrounded Tb^{3+} ions. In this case, the 325 nm light could stimulate the $4f^75 d^1 \rightarrow {}^9\text{D}_J$ transitions of Tb^{3+} ions. Such effect of the local field can be achieved for Tb^{3+} ions situated in distorted ZnO matrix as well as in the Tb-rich phases.

The quenching of Tb-related PL emission in the film grown on sapphire substrate upon its annealing can be caused by the decrease of Tb content in ZnO columns due to Tb segregation in Tb-rich phases. Besides, lower PL efficiency of Tb^{3+} ions situated in Tb-rich phase compared to that in ZnO columns can be governed by a concentration quenching effect.

The PL spectra of the AD and 600 °C annealed films recorded under excitation by 488 nm light demonstrate the Tb-related bands only, while the PL spectra of the films annealed at 900 °C show the additional set of PL bands caused by ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$ transition of Eu³⁺ ions (Fig. 6, Table 1). Since 488 nm light corresponds to resonant excitation of Tb³⁺ ions, the appearance of Eu³⁺ -related bands is obviously explained by an energy transfer from Tb³⁺ to Eu³⁺ ions.



Fig. 5. PL spectra of the films annealed at 900 °C recorded under 325 nm light excitation (a), PL spectra of as-deposited (AD) and 600° and 900 °C annealed films on Si (b) and Al_2O_3 (c) substrates recorded under 275 nm light excitation.

It is interesting that the shape of Eu^{3+} PL spectra depends on the substrate nature. In the case of Si substrate, they consist of several bands of different widths in the ranges of 580–630 and 646–660 nm. Some of the bands are very narrow (centered at 580.4, 587.7, 592.2, 610.0, 611.3, 629.2, 655.5 nm), while the others (peaked at 578.0, 585.6, 592.4, 597.0, 615.2, 622.6, 626.3, 653.3, 704.7 nm) have essentially larger widths. At the same time, for the film deposited on Al₂O₃, only the narrow lines are detected in PL spectra.

A comparison of the PL spectra excited by 488 and 325 nm light (Figs. 5 and 6) of the films annealed at 900 °C shows that only the most intense narrow line at 611.3 nm caused by ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions of Eu³⁺ ion is observed under UV excitation. Moreover, this line in the PL spectrum recorded under 325 nm laser excitation (insert in Fig. 6) demonstrates the same spectral position and close halfwidth as in the spectrum under 488 nm laser excitation.

3.4. IR reflection study

The specular IR reflection $(R(\nu))$ spectra of the films investigated are shown in Fig. 7 within the 100-1000 cm⁻¹ spectral range. The variation of the maximal $R(\nu)$ with annealing temperature in the film on Si substrate is caused by the presence of plasmon-phonon interaction between the film and substrate observed in the range of residual rays inherent to ZnO material (Fig. 7a). It should be noted that the variation of the sample orientation in the respect of polarized illumination affected negligibly the $R(\nu)$ spectral shape, which confirmed the orientation $\vec{E} \perp \vec{c}$ of (Tb,Eu) co-doped ZnO films. The peak position of the $R(\nu)$ maximum for the films grown on Si substrate is observed at $\nu = 411-412$ cm⁻¹ that corresponds to the frequency of ZnO TO



Overview of the ${\rm Eu}^{3+}$ transitions observed in the PL spectra of the films annealed at 900 °C.

	Transition	Peak position of narrow PL lines, nm	Peak position of wide PL lines, nm
1	${}^{5}D_{0} \rightarrow {}^{7}F_{0}$	580.4	578.0
2	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	587.7,	585.6,
		592.2	592.4,
			597.0
3	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	610.0,	615.2,
		611.3,	622.6,
		629.2	626.3
4	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	655.5	653.3
5	${}^{5}D_{0} \rightarrow {}^{7}F_{4}$		703.2,
			704.7,
			706.2
			706.2

phonon. The shape of the R(v) spectra and appearance of several features for the films grown on Al₂O₃ substrate (Fig. 7b) is determined by the overlapping of the ranges of residual rays of ZnO and Al₂O₃ [25].

The $R(\nu)$ spectra were simulated in the range of residual rays of ZnO and corresponding substrates using the approach described in earlier works [25,37–39,40] operating with a half-infinite substrate/film/air structure.

The model of dielectric permittivity with additive contribution of active optical phonons (ν_T) and plasmons (ν_p) in the ZnO film and Si substrate was considered [37–40]:



Fig. 6. Micro-PL spectra of the AD, 600° and 900 °C annealed films grown on Si (a) and Al₂O₃ (b) substrates excited with 488 nm laser line. The insert in (a) shows the micro-PL spectra of the (Tb, Eu)-ZnO/Si film annealed at 900 °C recorded under excitation with 488 nm and 325 nm laser lines in the 600–635 nm range.



Fig. 7. Experimental specular IR reflection spectra of the films grown on Si (a) and Al_2O_3 (b) substrates measured before and after annealing at 600 and 900 °C (symbols). The solid lines represent the fitting of experimental data.

$$\varepsilon_{j}(\nu) = \varepsilon_{lj}(\nu) + i\varepsilon_{2j}(\nu) = \varepsilon_{\infty j} + [\varepsilon_{\infty j}(\nu_{Lj}^{2} - \nu_{Tj}^{2})]/[\nu_{Tj}^{2} - \nu^{2} - i\nu\gamma_{fj}] - (\nu_{pj}^{2}\varepsilon_{\infty j})/[\nu(\nu + i\gamma_{pj})],$$
(1)

where v_{Lj} , v_{Tj} are the frequencies of LO and TO phonons in the film and substrate; γ_{fj} is the damping coefficient of optical phonons in the film and substrate; γ_{pj} and v_{pj} are the damping coefficient and plasmon resonance frequency in the film, respectively. For ZnO film, a single-os-cillator model for the orientation $\vec{E} \perp \vec{c}$ was taken into account.

For Al₂O₃ substrate, the dielectric permittivity was considered as

$$\varepsilon(\nu) = \varepsilon_{\infty} + \sum_{i=1}^{4} \frac{\Delta \varepsilon_i \nu_{Ti}^2}{\nu_{Ti}^2 - \nu^2 + i\nu\gamma_{fi}}$$
(2)

where ε_{∞} is the high frequency dielectric constant of Al₂O₃ for $\vec{E} \perp \vec{c}$ orientation; $\Delta \varepsilon_i$ is the strength of *i*th-oscillator; ν_{Ti} is the frequency of TO vibration of *i*th-oscillator; γ_{fi} is the damping constant of *i*th-oscillator.

To simulate IR spectra of the samples, the parameters of ZnO, Si and Al_2O_3 referred in Refs. [37–40] were used. The best fitting of experimental data was obtained using the parameters presented in Table 2 along with the calculated concentration (n_0) and mobility (μ) of free carriers as well as the conductivity (σ) of the films.

4. Discussion

4.1. The model of Tb-related emission centers

The revealed correlations between the intensity of Tb-related PL and some other optical and electrical characteristics allow proposing the model of Tb-related emission centers. Firstly, the shift of the E_2^{low} peak position shows that Tb incorporates into ZnO in substitutional position. Secondly, the PL intensity in as-deposited films correlates with the intensity of the $qA(E)_1(LO)$ mode. The latter testifies to the generation of defects in the oxygen sublattice. In turn, the decrease of Tb-related PL intensity under annealing correlates with the decrease of $qA(E)_1(LO)$ mode intensity (Figs. 2 and 4). Therefore, it can be supposed that Tbrelated emission center includes the substitutional defect Tb_{Zn} and defect in oxygen sublattice. The latter can arise to compensate excess charge of $\mathrm{Tb}^{3\,+}$ ions. Similarly, the increase of Tb-related emission caused by Li co-doping of ZnO was explained by compensation of excess charge of Tb_{Zn}^{3+} by Li_{Zn} acceptor [7,12,23,24]. In our case, this compensating acceptor defect in oxygen sublattice could be interstitial oxygen (O_i). Thus, Tb-related emission center can be considered rather as the complex including Tb_{Zn} and O_i than as only Tb_{Zn} in regular lattice. It should be noted the complexes of RE ions with oxygen (namely, clusters YbO₆ that are not alligned with ZnO matrix) were also proposed to be responsible for Yb-related emission in ZnO doped with Yb

Table 2			
Parameters of the films e	extracted by the fitting	of specular I	R spectra

Sample		Parameters					
		$\nu_{\rm p}$, cm ⁻¹	γ_p,cm^{-1}	$\gamma_{\rm f},cm^{-1}$	n ₀ ,cm ⁻³	Conductivity σ , $\Omega^{-1} \cdot cm^{-1}$	Mobility μ , cm ² /(V·s)
(Tb,Eu)-ZnO on Si substrate	AD	1150	880	18	$1.52 imes 10^{19}$	619	25.4
	$T_{A} = 600 \ ^{o}C$	1200	800	3	$1.65 imes 10^{19}$	742	28.0
	$T_{A} = 900 \ ^{o}C$	750	650	32	$6.50 imes 10^{18}$	580	56
(Tb,Eu)-ZnO on Al ₂ O ₃ substrate	AD	250	350	25	$7.19 imes10^{17}$	73	64
	$T_{A} = 600 \ ^{o}C$	380	2300	25	$1.66 imes 10^{18}$	26	10
	$T_A=900\ ^oC$	950	2650	25	$1.04 imes 10^{19}$	-	8

[41].

The appearance of defects in oxygen sublattice apparently occurs via formation of a pair of defects including O_i acting as acceptor and oxygen vacancy (V_O). The latter is known to be a deep donor in ZnO [42] that does not ionized at room temperature. Therefore, incorporation of Tb³⁺ ion into ZnO lattice should result in the decrease of free carrier concentration due to acceptor O_i formation. The higher the concentration of Tb-related emission centers, the lower the free carrier concentration.

This assumption is confirmed by the estimate of free electron concentration n_0 in the films obtained from IR reflection data. The results of simulation show that concentration of free electrons in the as-deposited film grown on Si substrate is higher than in the film deposited on Al₂O₃ ($n_0 \sim 10^{19} \text{ cm}^{-3}$ in the case of Si substrate against $n_0 \sim 10^{18} \text{ cm}^{-3}$ in the case of Al₂O₃). This is in agreement with the higher intensity of Tb-related emission in the AD film on Al₂O₃ substrate (Fig. 4a, Table 2).

Thermal treatment does not change significantly the n_0 value in the film grown on Si substrate (Table 2). However, an annealing of the film on Al₂O₃ substrate causes the increase of the n_0 value. Finally, for the film annealed at 900 °C, it reaches the same n_0 value as it was determined for the AD film on Si substrate. The increase of the n_0 upon annealing correlates with the decrease of Tb³⁺-related PL intensity. The latter is apparently caused by RE ions segregation from ZnO host (Fig. 4a and c). As a consequence, this results in the annihilation of the O_i-V_O defects and the increase of free carrier concentration.

The results of the PL and electrical investigations are consistent qualitatively with the proposed model of Tb-related emission centers. Some quantitative inconsistencies can be due to errors in the estimate. For example, the XRD data show that annealing at 900 °C stimulates formation of zinc silicate dielectric layer at the (Tb, Eu)-ZnO/Si interface. This layer causes the decrease of specular IR reflection intensity that affects the n₀ estimation in the film and can result in underestimated n₀ values.

4.2. Tb^{3+} -Eu³⁺ energy transfer

Since the Eu³⁺-related emission is not observed in the PL spectra of the AD and annealed at 600 °C films, we can conclude that the energy transfer from Tb³⁺ to Eu³⁺ is not efficient in ZnO host. The reason can be the low Eu concentration in the film because in such case Eu dopant can be present predominantly in +2 charge state of Eu_{Zn} defects [43]. The Eu³⁺-related emission appears only upon annealing at 900 °C when additional phases are generated. The XRD study shows that one of these phases is terbium oxide that is formed in the films on both types of substrate (Fig. 1). Another one is the Zn₂SiO₄ observed in the film on Si substrate only (Fig. 1).

Because the formation of Tb oxide phase is a common feature for the films on the substrates of both types, the narrow Eu^{3+} -related emission bands can be ascribed to the Eu^{3+} ions situated in the crystallized Tb oxide. It is apparent that in this phase, the distance between Tb^{3+} and Eu^{3+} ions is short since it is determined by the lattice constant. Thus, energy transfer, including Dexter mechanism requiring a distance close to 1 nm, can occur. Taking into account +4 charge state of terbium in TbO_2 and +3 in Tb_2O_3 , the phase in which the energy transfer from Tb^{3+} and Eu^{3+} ions takes place is Tb_2O_3 .

The narrow Eu^{3+} PL line at 611.3 nm recorded under UV excitation is rather originating from the Tb oxide phase than from ZnO (Figs. 5 and 6). In fact, it is observed only when the Tb oxide phase is formed, and both spectral position and halfwidth of this line are the same under 325 and 488 nm light excitation. In this case, the UV excitation most likely corresponds to band-to-band absorption in Tb oxide crystal phase (the band gap of Tb₂O₃ is about 3.8 eV) with subsequent energy transfer to Eu^{3+} ion.

Since the Eu³⁺ related PL bands of higher widths are observed for Si substrate only, they can be ascribed to the ions localized in some silicate

phase. The XRD patterns reveal the Zn_2SiO_4 formed in the film on the Si substrate upon the annealing at 900 °C. Therefore, it is naturally to assume that these PL bands are caused by energy transfer from Tb^{3+} to Eu^{3+} ions in Zn_2SiO_4 phase. However, the peak position of Eu^{3+} related PL bands differs from those reported for Eu^{3+} in Zn_2SiO_4 [44]. Therefore, we can't exclude that these bands originate from other silicate phases, namely RE-oxide silicate phases, formed upon the annealing. In this case, the energy transfer can be facilitated due to the accumulation of impurities at the interface film/substrate [26], which results in the decrease of the distance between Tb and Eu ions. It should be noted that formation of Tb,Eu silicates (oxiapatites) in this fims has been proved by transmittion electron microscopy. These results will be presented in another paper.

5. Conclusion

The effect of conventional annealing at 600 and 900 °C on the optical and electrical properties of Tb and Eu co-doped ZnO films deposited by magnetron sputtering on Si and Al_2O_3 substrates was investigated. It is shown that incorporation of Tb and Eu ions in ZnO host is accompanied by the formation of intrinsic defects in oxygen sublattice. The as-deposited films demonstrate Tb^{3+} -related PL bands and do not show any Eu-related emission. The efficiency of Tb^{3+} PL emission for the film on Al_2O_3 substrate is higher than that for the film on Si. On the contrary, the free carrier concentration evaluated from the IR reflection spectra is found to be higher for (Tb,Eu)-ZnO/Si film.

The XRD study shows that annealing at 900 °C results in formation of crystalline terbium oxide phase in the films of both types which indicates Tb out-diffusion from ZnO. Besides, the formation of the silicate phase in the film on Si substrate was observed.

In the PL spectra, the decrease of Tb^{3+} -related PL occurs under annealing. Simultaneously, the free carrier concentration increases. These changes are more pronounced in the film on Al₂O₃ substrate and can be assigned to Tb segregation accompanied by intrinsic defect annihilation. It is assumed that Tb^{3+} emitting centers are the complexes including Tb^{3+} substitutional and oxygen interstitial. The higher emission intensity in the film on Al₂O₃ substrate as compared with that on Si substrate correlates with the largest amount of intrinsic defects, thus testifying to the higher content of Tb^{3+} emission centers.

It is shown that thermal annealing at 900 °C leads to an energy transfer from Tb^{3+} to Eu^{3+} . The annealing results in the appearance of the set of narrow Eu-related bands in the film on Al_2O_3 substrate and two sets of the bands (narrow and wide) in the film on Si substrate. It is proposed that the narrow lines are originated from RE ions located in crystalline Tb_2O_3 , while the wide bands are connected with silicate phase. Effective energy transfer in additional phases is assigned to the decrease of distance between Tb and Eu ions (in particular, in silicate phase this is due to RE ions accumulation in it).

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References

- [1] Y.K. Mishra, G. Modi, V. Cretu, V. Postica, O. Lupan, T. Reimer, I. Paulowicz, V. Hrkac, W. Benecke, L. Kienle, R. Adelung, Direct growth of freestanding ZnO tetrapod networks for multifunctional applications in photocatalysis, UV photodetection, and gas sensing, ACS Appl. Mater. Interfaces 7 (2015) 14303–14316 https://doi.org/10.1021/acsami.5b02816.
- [2] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Optically pumped lasing of ZnO at room temperature, Appl. Phys. Lett. 70 (1997) 2230–2232 https://doi.org/10.1063/1.118824.
- [3] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Room-temperature ultraviolet nanowire nanolasers, Science 292 (2001) 1897–1899

https://doi.org/10.1126/science.1060367.

- [4] V. Kumar, O.M. Ntwacaborwa, H.C. Swart, Deep level defect correlated emission and Si diffusion in ZnO:Tb³⁺ thin films prepared by pulsed laser deposition, J. Colloid Interface Sci. 465 (2016) 295–303 https://doi.org/10.1016/j.jcis.2015.12. 007.
- [5] V. Kumar, O.M. Ntwaeaborwa, T. Soga, V. Dutta, H.C. Swart, Rare earth doped zinc oxide nanophosphor powder: a future material for solid state lighting and solar cells, ACS Photonics 4 (2017) 2613–2637 https://doi.org/10.1021/acsphotonics. 7b00777.
- [6] R. Krishna, D. Haranath, S.P. Singh, H. Chander, A.C. Pandey, D. Kanjilat, J. Mater. Sci. 42 (2007) 10047–10051 https://doi.org/10.1007/s10853-007-2053-4.
- [7] Y. Liu, W. Luo, R. Li, G.K. Liu, M.R. Antinio, X. Chen, Optical spectroscopy of Eu³⁺ doped ZnO nanocrystals, J. Phys. Chem. C 112 (2008) 686–694 https://doi.org/10. 1021/jp077001z.
- [8] A. Ishizumi, Y. Kanemitsu, Structural and luminescence properties of Eu-doped ZnO nanorods fabricated by a microemulsion method, Appl. Phys. Lett. 86 (2005) 253106 https://doi.org/10.1063/1.1952576.
- [9] M. Wang, C. Huang, Z. Huang, W. Guo, J. Huang, H. He, H. Wang, Y. Cao, Q. Liu, J. Liang, Synthesis and photoluminescence of Eu-doped ZnO microrods prepared by hydrothermal method, Opt. Mater. 31 (2009) 1502–1505 https://doi.org/10.1016/ j.optmat.2009.02.009.
- [10] T. Pauporte, F. Pelle, B. Viana, P. Aschehoug, Luminescence of nanostructured Eu3+/ZnO mixed films prepared by electrodeposition, J. Phys. Chem. C 111 (2007) 15427–15432 https://doi.org/10.1021/jp0747860.
- [11] S.M. Ahmed, P. Szymanski, M.A. El-Sayed, Y. Badr, L.M. El-Nadi, The photoluminescence properties of undoped and Eu-doped ZnO thin film grown by RF sputtering on sapphire and Si substrates, Appl. Surf. Sci. 359 (2015) 356–363 https://doi.org/10.1016/j.apsusc.2015.10.151.
- [12] L. Chen, J. Zhang, X. Zhang, F. Liu, X. Wang, Optical properties of trivalent europium doped ZnO:Zn phosphor under indirect excitation of near-UV light, Opt. Express 16 (2008) 11795–11801 https://doi.org/10.1364/OE.16.011795.
- H. Akazawa, H. Shinojima, Energy dissipation channels affecting photoluminescence from resonantly excited Er³⁺ ions doped in epitaxial ZnO host films, J. Appl. Phys. 117 (2015) 155303 https://doi.org/10.1063/1.4918365.
- [14] D. Wang, G. Xing, M. Gao, L. Yang, J. Yang, T. Wu, Defect-mediated energy transfer in red-light-emitting Eu-doped ZnO nanowire arrays, J. Phys. Chem. C 115 (2011) 22729–22735 https://doi.org/10.1021/jp204572v.
- [15] H. Yu, L. Xia, X. Dong, X. Zhao, Preparation and luminescent characteristic of Eu₂O₃-ZnO/(SBA-15) composite materials, J. Lumin. 158 (2015) 19–26 https://doi. org/10.1016/j.jlumin.2014.09.022.
- [16] L. Yang, Zh Jiang, J. Dong, A. Pan, X. Zhuang, The study the crystal defect-involved energy transfer process of Eu³⁺ doped ZnO lattice, Mater. Lett. 129 (2014) 65–67 https://doi.org/10.1016/j.matlet.2014.04.191.
- [17] L. Luo, F.Y. Huang, G.J. Guo, P.A. Tanner, J. Chen, Y.T. Tao, J. Zhuo, L.Y. Yuan, S.Y. Chen, Y.L. Chueh, H.H. Fan, K.F. Li, K.W. Cheah, Efficient doping and energy transfer from ZnO to Eu³⁺ ions in Eu³⁺-doped ZnO nanocrystals, J. Nanosci. Nanotechnol. 12 (2012) 2417–2423 https://doi.org/10.1166/jnn.2012.5779.
- [18] H.J. Lozykowski, Kinetics of luminescence of isoelectronic rare-earth ions in III-V semiconductors, Phys. Rev. B 48 (1993) 17758–17769 https://doi.org/10.1103/ PhysRevB.48.17758.
- [19] Y. Zhang, Y. Liu, L. Wu, E. Xie, J. Chen, Photoluminescence and ZnO–Eu³⁺ energy transfer in Eu³⁺-doped ZnO nanospheres, J. Phys. D Appl. Phys. 42 (2009) 085106https://doi.org/10.1088/0022-3727/42/8/085106.
- [20] E. Nakazawa, S. Shionoya, Energy transfer between trivalent rare earth ions in inorganic solids, J. Chem. Phys. 47 (1976) 3211–3219 https://doi.org/10.1063/1. 1712377.
- [21] C. Davesnne, A. Ziani, C. Labbe, P. Marie, C. Frilay, X. Portier, Energy transfer mechanism between terbium and europium ions in zinc oxide and zinc silicates thin films, Thin Solid Films 553 (2014) 33–37 https://doi.org/10.1016/j.tsf.2013.11. 122.
- [22] E. Pavitra, G. Seeta Rama Raju, Yeong Hwan Ko, Jae Su Yu, A novel strategy for controllable emission from Eu³⁺ or Sm³⁺ ions co-doped SrY₂O₄:Tb³⁺ phosphors, Phys. Chem. Chem. Phys. 14 (2012) 11296–11307 https://doi.org/10.1039/ C2CP41722G.
- [23] R.S. Ningthoujam, N.S. Gajbhiye, A. Ahmed, S.S. Umre, S.J. Sharma, Re-dispersed Li⁺ and Eu³⁺ co-doped nanocrystalline ZnO: luminescent and EPR study, J. Nanosci. Nanotechnol. 8 (2008) 3059–3062 https://doi.org/10.1166/jnn.2008. 152.
- [24] D. Xue, J. Zhang, C. Yang, T. Wang, PL and EL characterization of ZnO:Eu³⁺,Li films

derived by sol-gel process, J. Lumin. 128 (2008) 685–689 https://doi.org/10.1016/ j.jlumin.2007.11.077.

- [25] N. Korsunska, L. Borkovska, Yu Polischuk, O. Kolomys, P. Lytvyn, I. Markevich, V. Strelchuk, V. Kladko, O. Melnichuk, L. Melnichuk, L. Khomenkova, C. Guillaume, X. Portier, Photoluminescence, conductivity and structural study of terbium doped ZnO films grown on different substrates, Mater. Sci. Semicond. Process. 94 (2019) 51–56 https://doi.org/10.1016/j.mssp.2019.01.041.
- [26] C. Guillaume, C. Labbe, C. Frilay, J.-L. Doualan, F. Lemarie, L. Khomenkova, L. Borkovska, X. Portier, Thermal treatments and photoluminescence properties of ZnO and ZnO:Yb films grown by magnetron sputtering, Phys. Status Solidi A 216 (2018) 1800203 https://doi.org/10.1002/pssa.201800203.
- [27] A. Ziani, C. Davesnne, C. Labbé, J. Cardin, P. Marie, C. Frilay, S. Boudin, X. Portier, Annealing effects on the photoluminescence of terbium doped zinc oxide films, Thin Solid Films 553 (2014) 52–57 https://doi.org/10.1016/j.tsf.2013.11.123.
- [28] Powder Diffraction File, Card 36-1451, Joint Committee on Powder Diffraction Standards, ICDD, Newtown Square (PA), 2001.
- [29] A. Zhao, T. Luo, L. Chen, Y. Liu, X. Li, Q. Tang, P. Cai, Y. Qian, Synthesis of ordered ZnO nanorods film on zinc-coated Si substrate and their photoluminescence property, Mater. Chem. Phys. 99 (2006) 50–53 https://doi.org/10.1016/j. matchemphys.2005.10.013.
- [30] R.H. Callender, S.S. Sussman, M. Selders, R.K. Chang, Dispersion of Raman cross section in CdS and ZnO over a wide energy range, Phys. Rev. B 7 (1973) 3788–3798 https://doi.org/10.1103/PhysRevB.7.3788.
- [31] S. Sahoo, V. Sivasubramanian, S. Dhara, A.K. Arora, Excitation energy dependence of electron-phonon interaction in ZnO nanoparticles, Solid State Commun. 147 (2008) 271–273 https://doi.org/10.1016/j.ssc.2008.06.002.
- [32] Y.M. Hu, C.Y. Wang, S.S. Lee, T.C. Han, W.Y. Chou, G.J. Chen, Identification of Mn related Raman modes in Mn doped ZnO thin films, J. Raman Spectrosc. 42 (2011) 434–437 https://doi.org/10.1002/jrs.2695.
- [33] J.M. Calleja, M. Cardona, Resonant Raman scattering in ZnO, Phys. Rev. B 16 (1977) 3753–3761 https://doi.org/10.1103/PhysRevB.16.3753.
- [34] A. Hastir, R.L. Opila, N. Kohli, Z. Onuk, B. Yuan, K. Jones, V. Ravi, C. Singh, Deposition, characterization and gas sensors application of RF magnetron-sputtered terbium-doped ZnO films, J. Mater. Sci. 52 (2017) 8502–8517 https://doi.org/10. 1007/s10853-017-1059-9.
- [35] A. Hastir, N. Kohli, R.C. Singh, Comparative study on gas sensing properties of rare earth (Tb, Dy and Er) doped ZnO sensor, J. Phys. Chem. Solids 105 (2017) 23–34 https://doi.org/10.1016/j.jpcs.2017.02.004.
 [36] P. Dorenbos, The 4fⁿ 4fⁿ⁻¹5d transitions of the trivalent lanthanides in halogen-
- [36] P. Dorenbos, The 4fⁿ→4fⁿ⁻¹5d transitions of the trivalent lanthanides in halogenides and chalcogenides, J. Lumin. 91 (2000) 91–106 https://doi.org/10.1016/ S0022-2313(00)00197-6.
- [37] O.V. Melnichuk, L.Yu Melnichuk, N.O. Korsunska, L.Yu Khomenkova, YeF. Venger, Optical and electrical properties of Tb–ZnO/SiO₂ structure in the infrared spectral interval, Ukrainian J. Phys. 64 (2019) 431–438 https://doi.org/10.15407/ujpe64. 5.434.
- [38] O. Melnichuk, L. Melnichuk, B. Tsykaniuk, Z. Tsybrii, P. Lytvyn, C. Guillaume, X. Portier, V. Strelchuk, Ye Venger, L. Khomenkova, N. Korsunska, Investigation of undoped and Tb-doped ZnO films on Al₂O₃ substrate by infrared reflection method, Thin Solid Films 673 (2019) 136–140 https://doi.org/10.1016/j.tsf.2019.01.028.
- [39] E.F. Venger, A.V. Melnichuk, L.Yu Melnichuk, JuA. Pasechnik, Anisotropy of ZnO single crystal reflectivity in the region of residual rays, Phys. Status Solidi B 188 (1995) 823–831 https://doi.org/10.1002/pssb.2221880226.
- [40] E.F. Venger, A.V. Melnichuk, JuA. Pasechnik, E.I. Sukhenko, IR spectroscopy of the zinc-oxide-on-sapphire structure, Ukrainian J. Phys. 42 (1997) 1357–1360.
- [41] R. Ratajczak, S. Prucnal, E. Guziewich, C. Mieszczynsli, D. Snigurenko, M. Stachowicz, W. Skorupa, A. Turos, The photoluminescence response to structural changes of Yb implanted ZnO crystals subjected to non-equilibrium processing, J. Appl. Phys. 121 (2017) 075101https://doi.org/10.1063/1.4976207.
- [42] Ü. Özgür, YaI. Alivov, C.I. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, H. Morcos, A comprehensive review of ZnO materials and devices, J. Appl. Phys. 98 (2005) 04130https://doi.org/10.1063/1.1992666.
- [43] J. Petersen, C. Brimont, M. Gallert, G. Schmerber, P. Gilliot, C. Ulhaq-Bouillet, J.-L. Rehspringer, S. Colis, C. Becker, A. Slaoui, A. Dinia, Correlation of structural properties with energy transfer of Eu-doped ZnO thin films prepared by sol-gel process and magnetron reactive sputtering, J. Appl. Phys. 107 (2010) 123522 https://doi.org/10.1063/1.3436628.
- [44] A. Patra, G.A. Baker, S.N. Baker, Synthesis and luminescence study of Eu³⁺ in Zn₂SiO₄ nanocrystals, Opt. Mater. 27 (2004) 15–20 https://doi.org/10.1016/j. optmat.2004.01.003.