# Correlations between the structural transformations and concentration quenching effect for RE-implanted ZnO systems.

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## Abstract

In this paper, we present optical, structural and electrical studies of the phenomenon called concentration quenching effect occurring in ZnO doped with Rare Earth (RE) ions. For this purpose, the ZnO epitaxial layers grown by the Atomic Layer Deposition (ALD) are doped by ion implantation of Yb and Er elements with different fluencies ranging from  $5 \times 10^{13}$  to 1×10<sup>16</sup>/cm<sup>2</sup>. In order to activate optically implanted RE and remove defects, the postimplantation thermal annealing was performed at 800°C for 10 min in O<sub>2</sub> atmosphere using Rapid Thermal Annealing (RTA) system. Two-step processing samples, before and after annealing, were evaluated by Rutherford Backscattering Spectrometry (RBS/c) to investigate the damage build-up process in the ZnO lattice after RE ion bombardment and the lattice site location of RE. The annealed samples were examined using the photoluminescence (PL) spectroscopy and Hall effect measurements. Our studies show that the luminescence quenching effect, as well as electrical resistivity response to increasing RE concentration, are strongly connected with structural transformations threshold due to defects accumulation. It suggests that only during structural transformations the RE-ion centers are sufficiently close together to be able to interact and transfer the excitation energy between each other increasing ipso facto the probability to lose the excitation energy by non-radiative processes. Moreover, in contrast to the popular belief, that the concentration quenching effect in RE-doped ZnO depends strongly on the kind of RE-doped ion, the presented results do not provide any evidence to support such a theory.

### 1. Introduction

Even though the research focusing on ZnO started many decades ago, this material as a semiconductor with a wide and direct bandgap ( $\sim 3.37 \text{ eV}$  at T = 300 K) has been experiencing a renewed interest due to its extensive potential application spectrum in microelectronics,

organic electronics, biosensors and spintronics [1-4]. However, the high exciton binding energy (60 meV) of this material predestines it for optical and optoelectronic applications such as lightemitting diodes and phosphors as well [5-7]. ZnO received also a large interest because of easy and cheap technology of the growth of ZnO crystals and films. Especially interesting is the growth by the Atomic Layer Deposition (ALD) method [8], which might be perspective for industrial large-scale applications [9]. It is worth to note that the low-temperature ALD can be integrated with Organic Light-Emitting Devices (OLED's technology) developing very quickly last years [2,10-11], thus ALD can play a significant role in future competitive solutions based on organic electronics.

The spectrum of the light emission from ZnO is located in the violet-blue spectral range. The doping of ZnO with Rare Earth (RE) can modify optical properties of the material and tune the optical emission from UV to near infrared. RE elements have been successfully used in optics and optoelectronic applications of other materials [12-14]. They typically exhibit characteristic narrow emission lines in the ultra-violet, visible and infrared spectral regions that originate from the 4f intra-shell transitions. The 4f electron shell is highly localized, so the intra-shell transitions of the 4f electrons are only slightly affected by the host material. Nevertheless, the wide bandgap semiconductors are especially interesting as host materials because they are expected to overcome the temperature quenching effect appearing in other materials (e.g. in Si), resulting in an effective f shell resonant pumping [13-14].

Ion implantation is an attractive tool for doping of materials where the RE concentration and depth profile can be precisely controlled by selecting an appropriate ion fluence and energy, respectively [15]. Moreover, ion implantation is a strongly non-equilibrium process allowing an introduction of any kind of atoms into solids with a concentration well above solid solubility limits. It has also been found that PL intensity from RE implanted into the material is a few

times higher as compared to the same material with RE introduced during the growth process [16]. However, in the as-implanted stage, most of the RE-dopants in ZnO are optically inactive [17].

In order to get the optical activity of the RE-implanted ZnO system, the thermal annealing is necessary. The thermal treatment leads to the partial recovered of the crystal lattice, damage by RE low fluence implanted ZnO but is associated with a simultaneous process of RE diffusion and agglomeration on the sample surface due to the low solubility limit [17]. Therefore, a reasonable solution is a balance between the perfect recovery of the crystal and a stable RE profile using thermal annealing giving the best PL efficiency. The thermal annealing at 800°C for 10 min in O<sub>2</sub> atmosphere has been found to be optimal for ZnO:RE systems implanted at RT [17]. Important is, that the high-level of disorders above the plastic transformation threshold, and hence the created extended/complex defects cannot be removed by thermal annealing [18].

Interestingly, up to now, it was considered that the increase of the concentration of RE dopant in ZnO matrix decreases the luminescence intensity. This is mainly because the increasing energy transfer between the densely packed RE centers leads to an increase probability to lose the excitation energy through non-radiative processes [19]. This phenomenon called the concentration quenching effect in RE-doped ZnO has been only poorly investigated so far and the achieved results are quite inconsistent [20-21]. Benz et al. [22] demonstrated that 'optimum concentration' (concentration for the maximum luminescence intensity) poorly depend on the host matrix, but is strongly related to the kind of doped RE ion [23]. However, as was shown, even different preparation conditions of samples could influence a location of RE in ZnO matrix, resulting in the various local structure and different values of 'optimum concentration' [24-26]. Moreover, it was also found that an effective optical emission from RE ions strongly depends on chemical bonding with a surrounding crystal matrix, local arrangement, the symmetry and ligand field strength around the RE ion [27].

In this paper, we present and discuss the effect of RE concentration on structural, optical and electrical properties of the ZnO films, aimed at the comprehensive studies of the quenching phenomenon. In our case, high-quality ZnO-ALD films were doped by ion-implantation with the different fluencies of Yb and Er ions. The efficient photoluminescence at room temperature was recorded from such ZnO:RE systems separately in two spectral regions: the UV-visible region, originating from near band-gap and deep level emissions (NBE and DLE) as well as the infrared region due to characteristic emissions from intra-band transitions of Yb<sup>3+</sup> and Er<sup>3+</sup>. Our results show that the concentration quenching effect observed in the optical and electrical studies is strongly connected with the threshold of the plastic deformation, which occurs for doping concentrations of RE about  $1.5 \times 10^{15}$  at/cm<sup>2</sup>. Our studies also show that there is no significant difference between quenching phenomenon of Yb and Er ions, introduced to the ZnO matrix using ion implantation.

# 2. Experimental conditions

High-quality epitaxial ZnO [0001] films were grown on a commercial GaN/Al<sub>2</sub>O<sub>3</sub> substrate (Kyma Co.) by Atomic Layer Deposition (ALD) method [8, 28-30]. The growth processes were performed in a Savannah ALD system at 300°C. The ZnO layer was created as a result of a double-exchange chemical reaction between diethylzinc and water that takes place at the surface:

 $Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2C_2H_6$ 

The details of the growth process can be found in Ref. 31. The layer thickness was about  $1\mu m$ .

Next, the ZnO films were implanted at room temperature (RT) with 150 keV Yb or Er ions to the fluencies ranging from  $5 \times 10^{13}$  to  $1 \times 10^{16}$  at/cm<sup>2</sup> at 7° off the [0001] direction, in order to reduce the channeling effect. The Yb ions were implanted at the Institute of Electronic Materials Technology (ITME, Warsaw, Poland) using the ion implanter Balzers MBP 202RP, while the Er ions were implanted at the Ion Beam Centre, Helmholtz-Zentrum Dresden-Rossendorf (IBC/HZDR, Dresden), Germany using Danfysik 1090 ion implanter. The RE ion ranges (R<sub>p</sub>) and the depth of the maximum of the nuclear energy loss profiles (R<sub>pd</sub>), determined by SRIM simulations [32], are ~33 and ~23 nm, respectively, while the thickness of the whole modified layer is about 120 nm.

Due to the fact that directly after ion implantation the RE atoms remains mostly optically inactive [17] the RE-implanted layers were subsequently thermally annealed at 800°C for 10 min in oxygen ambient using RTA system (Accu Thermo AW-610 from Allwin21 Corporation) with high temperature growth rate (16 K/s). The time and temperature of annealing were selected on the basis of our previous experience with ZnO-ALD films implanted with Yb ions [17, 30].

Crystal structure quality, post-implanted damages and post-annealing structure recovery as well as the RE lattice site location before and after annealing were evaluated by the Channeling Rutherford Backscattering Spectrometry (RBS/c) [33-34] at the IBC/HZDR, Dresden, Germany, using 1.7 MeV He ions. The backscattered particles were detected by a silicon surface barrier detector at backscattering angle of 170 deg.

The optical properties of annealed ZnO implanted with RE were studied by the PL spectroscopy. For the sample excitation, a UV He-Cd laser with 325 nm wavelength and 8 mW power was used. The signal was detected at room temperature through a Jobin Yvon Triax 550 monochromator and two types of detector: a liquid nitrogen cooled InGaAs detector for

measurements in the IR region and a photomultiplier (Hamamatsu H7732-10) for the UVvisible region, both associated with a standard lock-in amplifier.

The resistivity as well as electron concentration and mobility of the annealed RE-implanted ZnO layers were obtained using the Hall effect measurements performed in the Van der Pauw geometry [35] on 10 mm x 10 mm samples using a RH2035 setup provided by PhysTech GmbH, equipped with a permanent magnet producing the magnetic field B = 0.426 T. The ohmic contacts to the ZnO films were obtained using e-beam evaporated Ti(100 Å)/Au(400 Å) bi-layer with indium soldered on the top.

# 3. Results and discussion

### **3.1 RBS/c analysis**

In the first step, the defect accumulation and defects transformations processes in ZnO implanted with Yb and Er were studied. **Figure 1** shows the typical RBS random and aligned spectra obtained for ZnO implanted with different fluences of RE ions. In such a case, fortunately, the Zn signals in the RBS spectra and the signal originating from RE are clearly separated, which enables independent study of ZnO and RE sublattices. The low energy part of the RBS spectra (up to 1370 keV) represents a signal of He-ions backscattered from Zn. The aligned spectra in this region illustrate lattice damage as a result of the ballistic nature of the implantation process, allowing the studies of irradiation defect evolution with increasing ion fluence. In turn, the high energy part (1400-1550 keV) represents a signal of He-ions backscattered from RE and the aligned spectra in this region reflect the behavior of RE in the ZnO matrix.

As can be seen in **Figure 1**, a comparison of the random and aligned RBS spectra in the high energy part leads to the conclusion that, after implantation, a part of implanted RE atoms is located in the substitutional lattice position. However, a substitutional fraction ( $f_s$ ), defined as

the relative amount of the impurity atoms occupying lattice site positions [33] for ZnO:RE system decreases as a function of increasing ion fluence. The numerically evaluated substitutional fractions of RE after subsequent implantations are presented in **Table 1**. The results of calculation indicate that for the fluences higher than  $2 \times 10^{15}$  /cm<sup>2</sup>, the process of rejection of RE ions to the interstitial positions is accelerated, but still about 30% of Yb atoms remain in Zn-substitutional positions along the [0001] direction. Significant difference in the behavior of Yb and Er ions in the ZnO matrix was not noticed.

Looking at the low energy region of the RBS/c spectra there is no visible change in the aligned spectra for low fluences of RE. Starting from the fluence of  $2.5 \times 10^{14}$  /cm<sup>2</sup> the small double-damage peak on the top of the dechanneling background appears and grows up to the fluence equal to  $1.5 \times 10^{15}$  /cm<sup>2</sup> without changing the energy position. Above the fluence of  $2 \times 10^{15}$  /cm<sup>2</sup> the damage peak keeps growing up and is shifted towards lower energy (i.e. higher depths). Such results clearly indicate that upon ion implantation the fluence above of  $1.5 \times 10^{15}$  /cm<sup>2</sup> a complicated defect structure has developed. The obtained lattice damage levels after implantation with both RE species are very similar.

The *McChasy* computer code [36-37] based on Monte Carlo simulations was used to analyze the damage depth profiles in the aligned RBS spectra for ZnO implanted with both: Yb and Er ions. The solid lines in **Figure 2** show the results of MC simulations performed as the best fit to the damage peaks assuming randomly displaced atoms (RDA) and extended defects such as: dislocations, dislocation loops, stacking faults, etc. All of the latter defects cause lattice distortions extending tens of unit cells, therefore are modeled as dislocations (DIS). That possibility of simulations using the mixture of defects constitutes the uniqueness of the *McChasy* program. The best fits have been obtained for RDA (solid lines) and DIS (dashed lines) defect distributions shown in **Figure 3a** and **3b**, respectively. In the RDA depth profiles, three regions of damages can be distinguished reflecting, characteristic for ZnO implanted with

heavy ions, atypical damage structure behavior. The deepest region (25-100 nm) is the typical damage peak (DP) related to the bulk defects after implantation. Although, as can be seen, the maximum of DP peak is located at about 40 nm and is deeper than indicated by theoretical calculations using the SRIM code [32]. In contrast, the first region (0-15 nm) corresponds to the atypical damage peak called intermediate peak (IP), which reflects disorder on the surface due to the oxygen loss [30]. Finally, the region between them (15-25nm from the surface), where the low damage level is observed, is connected with the maximum nuclear energy loss R<sub>pd</sub> calculated by SRIM code. Such a character of RDA depth profiles is connected with migration and agglomeration of the defects as has been already reported before for single ZnO crystals. A detailed description of the model can be found elsewhere [38]. Both RDA and DIS distributions are increasing as a function of ion fluences, but even after heavy-ion bombardment with fluences up to  $1 \times 10^{16}$  /cm<sup>2</sup>, which corresponds to about 100 dpa the amorphous level was not achieved. Moreover, the DIS defects are also created deeper (beyond the ion range) and the step-shift of DIS distributions to a higher depth for fluences above  $1.5 \times 10^{15}$  /cm<sup>2</sup> can be observed. It suggests, that one of the factors limiting the damage buildup in the ZnO material can be linked to dislocation mobility. However, it is worth emphasizing that our observations were performed in only one (0001) direction. The latest papers actually show that the defect accumulation process for a variety of axes is going in very different ways [39-40].

The maxima of RDA and DIS distributions form the defects accumulation curves presented in **Figure 4**. The defect accumulation and transformation in ion-implanted compound crystals is usually a complicated multistep process resulting in the formation of a mixture of different types of structural defects [38, 41-43]. In the case of ZnO-ALD films, two-steps accumulation process is observed, although as already mentioned, the amorphization level of the structure has not been achieved. Accumulation curves were fitted by the multistep damage accumulation

model (MSDA) [41]. As can be seen in Figure 4, the accumulation rate of both kinds of defects is very low in the low fluence region. Generally the dynamic annealing process i.e. defects migration allowing recombination, is considered to be a cause of this. However, it is only partially true, because our recent studies showed an increase of the strain along the c-axis with increasing ion fluencies due to basal dislocation loops growth [38, 43]. That kind of disorder (perpendicular to the c-axis) cannot be observed in RBS/c spectra measured in (0001) direction. As soon as the critical value of the stress is achieved, the plastic deformation in the implanted layer begins, leading to structural relaxation. In the case of ZnO-ALD films implanted with RE, the mentioned process starts with the ion fluence higher than  $2 \times 10^{14}$  /cm<sup>2</sup> and may be observed as a rapid increase in defect concentrations. Further increase of ion fluence leads to an increase of defects concentration up to the saturation level of about  $5 \times 10^{15}$  /cm<sup>2</sup>, which means that the defect structure transformation has been finished resulting in a creation of the new form of a defect. The plastic deformation edge position was evaluated for fluence of about  $1.5 \times 10^{15}$  /cm<sup>2</sup>, which corresponds to the values of ~ 8 dpa and ~0.14 at %. This process usually leads to the dislocation tangles, stacking faults and eventually to crystal mosaic and large defect clusters formations as well [43]. Such defects are resistant to thermal annealing [18]. There have been no noticed a significant difference in the accumulation processes of Yb and Er ions.

# 3.2 Optical analysis

The defects produced during ion implantation process quench most of luminescence from the ZnO sample. Moreover, RE-dopants in as-implanted ZnO are optically inactive. Therefore, the annealing is needed for structure recovery and dopant activation. The thermal treatment leads to the recovered of the crystal lattice, damage by RE low fluence implanted ZnO but is associated with a simultaneous process of RE diffusion and agglomeration on the surface of the sample due to the low solubility limit [17]. Thus, selected parameters of thermal annealing (RTA 10 min, 800°C, O<sub>2</sub> atmosphere) are a tradeoff between the perfect recovery of the crystal and a stable impurity

depth profile [17,18]. It is worth noting that the annealing in such conditions removes lattice damage in the near-surface region of ZnO [30].

In order to investigate the effect of RE-concentration inside ZnO on the PL emission intensity, the photoluminescence measurements for RE-ion implanted-annealed ZnO layer (hereafter called ZnO:RE system), were performed at room temperature for both studied ions. The PL spectra at two spectral regions: visible and near infrared (IR) were recorded.

Typical PL spectra measured in the visible region for the above-band gap excitation (325 nm) on an example of ZnO:Yb systems are shown in Figure 5. For comparison, the PL results obtained for undoped ZnO and after 10 min RTA are added. For undoped ZnO (Figure 5a) two peaks can be observed. One of them corresponds to the near-band-edge emission (NBE) at 380 nm from ZnO and the second broad peak with maximum at 520 nm, called deep-level emission (DLE) is due to native defects excitation. As can be seen in Figure 5a, the annealing process enhances mainly defects luminescence thus weakening the NBE. As was reported before the green luminescence in undoped ZnO is most commonly ascribed to zinc vacancies  $(V_{Zn})$  [44-45] (and oxygen vacancies, which are mostly annihilated during annealing in O<sub>2</sub> atmosphere [46]) as well as zinc antisites [24], red emission – to zinc vacancy clusters [46-47], while the responsibility for yellow band is frequently assigned to excessive oxygen (O<sub>i</sub>) [24, 46]. The RE implantation effectively suppresses both NBE and DLE but those lumienscence returns after annealing. Nevertheless, the observed NBE is weaker in implanted ZnO than for undoped ZnO after annealing. An increase of the implantation fluence further increases the quenching of the NBE and DLE. However, the shape of DLE peak is changing with increasing of RE fluences, showing the enhancing role of defects like Oi and/or VZn clusters. Besides, the influence of complexes of these defects and defects-related to RE for doped ZnO cannot be excluded as well [48-51].

The annealing process leads also to an optical activation of Yb<sup>3+</sup> and Er<sup>3+</sup>, which makes possible the observation the 4f transitions characteristic for both studies ions in the IR region. Because the used excitation energy is higher than the ZnO bandgap the RE ions are mostly excited indirectly. In the case of Yb<sup>3+</sup>, the main transition from the excited  ${}^{2}F_{5/2}$  to the  ${}^{2}F_{7/2}$ ground state of Yb<sup>3+</sup> give a sharp peak at 980 nm visible in Figure 6 Broad peaks situated between 1000 and 1040 nm correspond to the  $Yb^{3+}$  ion emission vibronic band  ${}^{2}F_{5/2}$  to the  ${}^{2}F_{7/2(n)}$ ; n=1,2,3,4) [52]. In the case of Er<sup>3+</sup> the PL emission at around 1.54  $\mu$ m, originating from the transition from the  $^4I_{13/2}$  to the  $^4I_{15/2}$  ground state of  $\mathrm{Er}^3$  was considered (PL spectra not shown here). For both studied ions, the emission intensity changed non-monotonically with the RE concentration in ZnO. Moreover, in Figure 6 the small blue shift of the main peaks of  $RE^{3+}$ and the change in the vibronic band emission region for the fluences above  $1.5 \times 10^{15}$  /cm<sup>2</sup> can be observed, which marks the changes of the local environment or/and symmetry of the host material [53-54] The relationships between the maximum of PL intensity, for  $Yb^{3+}$  at 980 nm, as well as  $Er^{3+}$  at 1534 nm, and the RE content are shown in in Figure 7. As can be seen, when the Yb fluence is lower than  $1.5 \times 10^{15}$  /cm<sup>2</sup> the PL intensity increase with the Yb content. For fluences higher than  $1.5 \times 10^{15}$  /cm<sup>2</sup> the PL intensity suddenly decreases, especially when the Yb content reaches  $2 \times 10^{15}$  /cm<sup>2</sup>. Further increase of the fluence leads surprisingly to an increase of the PL intensity, even though the damage level of the structure is very high. It indirectly may show that, due to the low solubility limits for RE ions in ZnO and mobility of atoms during annealing, a secondary phase of RE<sub>2</sub>O<sub>3</sub> or other RE-related clusters are formed for high RE fluence [46]. There is also a great possibility of locating RE ions in the mosaic boundary region in order to make optically active centers in ZnO [55]. For both studied ions, the character of such dose-dependences is similar. However, Figure 7 shows also some differences between the RE dose-dependences of the PL intensity for Yb and Er. In the case of Er ion, the inflection point seems to be for the little bit lower fluencies.

## **3.3** Electrical studies

Electrical measurements of the RE-implanted ALD-ZnO layers such as electrical resistivity confirm earlier observations concerning the behavior of RE-implanted ZnO material. The dependences of electrical resistivity of ZnO:Yb and ZnO:Er thin films as a function of the RE concentration measured by the Hall Effect is presented in Figure 8. Krajewski et al. have shown that the carrier concentration in our implanted ZnO layers is about  $n\sim 10^{18}$  /cm<sup>3</sup> [18]. As a result of the post-implantation RTA annealing, the carrier concentration increases and tends to stabilize, after 10 min RTA. It is usually assigned to the temperature-induced migration of RE ions from the substitutional positions in the Zn sublattice to the interstitial ones. The carrier concentration of ZnO:Yb systems as a function of the Yb fluence, reveal some dependences shown in Ref. [18], which is also reflected in the dose-dependence of resistivity shown in Figure 8. The resistivity of Yb implanted ZnO initially decreases rapidly from a  $3.2 \times 10^{-2} \Omega$ cm to  $2.8 \times 10^{-2} \Omega$ cm with increasing Yb fluence up to  $1.5 \times 10^{15}$  /cm<sup>2</sup>, above which increases gradually with the further increase of Yb fluence. A similar dependence of electrical resistivity of ZnO:Er systems with different Er concentrations is observed. The initial rapid decrease in resistivity up to the fluence  $1.5 \times 10^{15}$  RE ions/cm<sup>2</sup> again clearly indicates that most of the RE substitute Zn as donor dopant in the ZnO lattice and hence introducing the free electrons to the ZnO lattice [30]. Nevertheless, as structural studies have shown, the high doping concentration of RE in the ZnO lattice results in the interstitial RE ions in the ZnO matrix (additionally enhanced by annealing [17, 29]). Interstitial RE is in 3+ valence state, thus interstitial RE<sup>3+</sup> may be considered as acceptor-type defects. Moreover, PL spectra obtained from heavily implanted ZnO suggest the increase of the concentration of the other acceptors' defects such as O<sub>i</sub> and V<sub>Zn</sub> as well. All these are aimed to cause the compensation of free carriers, thus keeping the charge balance in the system and simultaneously results in an increase of resistivity above the fluence of  $1.5 \times 10^{15}$  /cm<sup>2</sup> with further the tendency to saturate. Such a hypothesis may also be found in the literature, describing similar studies [24, 55- 56].

# 4. Conclusions

In the paper, the influence of increasing concentration of RE-implanted into ALD-ZnO epitaxial layers on the structural, optical as well as electrical properties were thoroughly investigated. Our results demonstrate that the concentration quenching effect observed in the optical and electrical studies is connected with the threshold of the plastic deformation.

Our studies of the implantation process effect shown, that the defect accumulation in ionimplanted ZnO is a complicated multistep process leading to the transformation of structural defects to their new form. We have found that ion bombardment with a low fluence (below  $2 \times 10^{14}$  /cm<sup>2</sup>) does not cause the damage in (0001) direction, however as suggested in our previous works, the increase of stress along c-plane with increasing ions fluences was noticed. Consequently, interstitial atoms, small point clusters and dislocation loops in other than (0001) directions are formed. When the critical value of the stress has been achieved, plastic deformation due to the dislocation slip takes place leading to the formation of dislocation tangles, stacking faults, crystal mosaic as well as large defect clusters. These cluster defects act as the radiative centers, so most likely are related to  $RE^{3+}$ . However, the nature of these clusters needs to be further studied. For RE implanted ZnO-ALD films the threshold of such process (maximum of stress) was evaluated for the ion fluence about  $1.5 \times 10^{15}$  /cm<sup>2</sup>, which corresponds to the values of  $\sim 8$  dpa and this process seems to be completely finished for the fluencies above  $5 \times 10^{15}$  /cm<sup>2</sup>. After implantation, a part of implanted RE atoms is located in the substitutional lattice position in [0001] direction. However, a substitutional fraction decreases as a function of increasing ion fluence. Significant difference in the accumulation processes and behavior of Yb and Er ions in the ZnO matrix was not noticed.

An increase of stress and RE concentration with the increasing of RE ions fluence also contributes to an increase in the density of packed RE centers, which is highest when the critical value of stress is achieved. Consequently, the transfer energy between RE centers becomes easier, resulting in the enhanced probability of losing the excitation energy by non-radiative processes, thus reducing the  $RE^{3+}$  luminescence. Interestingly, above the plastic transformation threshold the PL intensity from  $RE^{3+}$  increases again as a function of ion fluencies with tend to saturate. It can be associated with the precipitations of RE into ZnO in cluster form (most likely connected with other native defects in the matrix) and/or their location in the mosaic boundary. Because of that the same luminance efficiency level for the fluencies of  $1 \times 10^{15}$  and  $5 \times 10^{15}$  /cm<sup>2</sup> was obtained. We have also shown that the plastic deformation leads also to strengthen the process of rejection of originally substitutional RE ion to the interstitial positions, which is usually connected with the change of RE the valence state from 2+ to 3+. Moreover, other acceptor-like defects such as O<sub>i</sub> and V<sub>Zn</sub> can appear. These changes seem to explain the characteristic course of the dependence of resistivity on the ion fluence.

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**Figure 1** Random and [0001] aligned RBS experimental spectra obtained for epitaxial ZnO layers implanted with different fluencies of Yb ions.



**Figure 2** Random and [0001] aligned RBS experimental spectra obtained for epitaxial ZnO layers implanted with different fluencies of Yb ions. Solid lines in the Figure are results of MC simulations made with the *McChasy* code.



Figure 3 Depth distributions of defects a) randomly displaced atoms (RDA), b) dislocation (DIS).



**Figure 4** Defect accumulation curves obtained for epitaxial ZnO-ALD layers implanted with different fluences of Yb and Er ions.



**Figure 5** PL spectra in the visible region for ALD-ZnO layers (a) virgin and (b) implanted with different fluences of Yb ions and annealed for 10 min at 800°C in an oxygen atmosphere.



**Figure 6** PL spectra in the IR region for ALD-ZnO layers implanted with different fluences of Yb ions and annealed for 10 min at 800°C in an oxygen atmosphere.



Figure 7 Dependence of PL intensity of  $RE^{3+}$  signals into ZnO:RE systems on different RE ions concentration.



Figure 8 Dependence of electrical resistivity of ZnO:RE system on different RE ions concentration.

Concentration of Yb [10 <sup>15</sup> at/cm <sup>2</sup> ]	χ <sub>min</sub> (Zn)	χ <sub>min</sub> (Yb)	fs
0	4.2	4.5	-
0.005	4.2	4.5	1.00
0.01	4.2	6.0	0.98
0.25	12.8	17.4	0.89
0.5	19.0	21.7	0.87
0.75	24.3	25.3	0.85
1	30.6	38.4	0.72
1.5	38.6	39.6	0.72
2	51.1	55.2	0.55
5	73.9	77.8	0.28
10	83.8	75.6	0.34

Table 1 Characteristic parameters for ZnO-ALD layers implanted with different Yb ions fluences.

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