



This work was carried out in whole or in part within the framework of the NOMATEN Center of Excellence, supported from the European Union Horizon 2020 research and innovation programme (Grant Agreement No. 857470) and from the European Regional Development Fund via the Foundation for Polish Science International Research Agenda PLUS programme (Grant No. MAB PLUS/2018/8).

This is a copy of the publication which appeared in: Applied Surface Science, vol 521 (2020) 146421, published on: 24 April 2020.

DOI: 10.1016/j.apsusc.2020.146421

Contents lists available at ScienceDirect





Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

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



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ARTICLE INFO

Keywords: Rare earth Ytterbium Erbium Implantation, radiation defects Quenching effect Rutherford Backscattering Spectrometry (RBS/ c) Photoluminescence (PL) PL Hall effect

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 epitaxial ZnO layers grown by the Atomic Layer Deposition (ALD) are doped by ion implantation with Yb and Er elements with fluencies ranging from 5×10^{13} to 1×10^{16} /cm². In order to activate optically the implanted RE and to remove defects, the post-implantation thermal annealing was performed at 800 °C for 10 min in the O2 atmosphere using a Rapid Thermal Annealing (RTA) system. Two-step processed 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 the electrical resistivity response to the increased RE concentration, are strongly connected with the threshold of the structural transformation due to defects accumulation. It suggests that 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 an assumption.

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 eV at T = 300 K) has been experiencing a renewed interest due to its extensive potential application spectrum in microelectronics, organic electronics, solar cells, biosensors and spintronics [1–5]. 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 [6–8]. ZnO received also a large interest because of the easy and cheap technology of the growth of ZnO crystals and films [9–11]. Especially interesting is the growth by the Atomic Layer Deposition (ALD) method [9], which might be a perspective for industrial large-scale applications [11–13]. It is worth noting that the low-temperature ALD can be integrated with Organic Light-Emitting Devices (OLED's technology), which recently develops very quickly [2,13–15]. Because of that ALD can play a significant role in future competitive solutions based on organic electronics.

The band-edge light emission from ZnO is located in the violet-blue spectral range. The doping of ZnO with Rare Earth (RE) can modify the 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 [16–17]. 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),

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https://doi.org/10.1016/j.apsusc.2020.146421

Received 13 February 2020; Received in revised form 27 March 2020; Accepted 3 April 2020 Available online 24 April 2020

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resulting in an effective resonant pumping of the f shell [17–18].

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 [19–22]. 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 [23]. However, in the as-implanted stage, most of the RE-dopants in ZnO are optically inactive [24], because of the damage of the crystal lattice caused by implantation.

In order to get the optical activity of the RE-implanted ZnO system, thermal annealing is necessary. The thermal treatment leads to the partial recovery of the crystal lattice damage caused by the RE implanted to ZnO. However, it is associated with a simultaneous process of RE diffusion and agglomeration on the sample surface due to the low solubility limit [24]. Therefore, a reasonable solution is to find appropriate conditions of thermal annealing, which assure a balance between the crystal lattice recovery and a stable RE profile. The thermal annealing at 800 °C for 10 min in O_2 atmosphere is the optimal for ZnO:RE systems implanted at RT [24]. However, it should be remembered that for high ion fluence, the plastic deformation threshold can be exceeded, which results in the creation of the extended complex defects that cannot be removed by any thermal annealing [25].

Moreover, it has been found that too high an increase of the concentration of RE dopant in ZnO matrix yields decreased luminescence intensity. This is mainly because the increasing energy transfer between the densely packed RE centers leads to an increased probability to lose the excitation energy through non-radiative processes [26]. This phenomenon, known as the concentration quenching effect, in RE-doped ZnO has been only poorly investigated so far and the achieved results are quite inconsistent [27–28]. Benz et al. [29] demonstrated that 'optimum concentration' (concentration for the maximum luminescence intensity) poorly depends on the host matrix, but is strongly related to the kind of doped RE ion [30]. However, as was shown, even different preparation conditions of samples could influence a location of RE in the ZnO matrix, resulting in the various local structure and different values of 'optimum concentration' [31-33]. 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 [34].

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 intraband transitions of Yb³⁺ and Er³⁺. 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 1.5×10^{15} at/cm². Our studies also show that there is no significant difference between the quenching phenomenon of Yb and Er ions, introduced to the ZnO matrix using ion implantation.

2. Experimental conditions

Epitaxial ZnO [0001] films were grown on a commercial GaN/Al_2O_3 substrate (Kyma Technologies) by Atomic Layer Deposition (ALD) method [9]. 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:

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

The details of the growth process can be found in Ref. [35]. The crystalline quality of virgin samples was evaluated by RBS/c and HRXRD. The reciprocal space maps (RSMs) made in the vicinity of chosen reciprocal lattice spots of the epitaxial layer and substrate crystals show that the Full Width at Half Maximum (FWHM) of the 00.2 reflection equals to 0.149°, while FWHM of the -1-1.4 reflection is 0.1055°. These values are very close to those obtained for the used GaN/Al₂O₃ substrate. The value of the crystalline quality parameter χ_{min} obtained from RBS/c measurements of ZnO-ALD films is about 4%, which is close to the value measured for a commercial single ZnO crystal (MaTecK GmbH). The results confirm the epitaxial quality of obtained films and were already published [22,36–38]. The layer thickness was about 1 µm.

Next, the ZnO films were implanted at room temperature (RT) with 150 keV Yb or Er ions to the fluencies ranging from 5 \times 10¹³ to 1 \times 10¹⁶ at/cm² 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_p) and the depth of the maximum of the nuclear energy loss profiles (R_{pd}), determined by SRIM simulations [39], are ~33 and ~23 nm, respectively, while the thickness of the whole modified layer is about 120 nm.

Since directly after ion implantation the RE atoms remain mostly optically inactive [24] the RE-implanted layers were subsequently thermally annealed at 800 °C for 10 min in oxygen ambient using a 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 based on our previous experience with ZnO-ALD films implanted with Yb ions [24,38].

Crystal structure quality, post-implantation 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) [40–41] at the IBC/HZDR, Dresden, Germany, using 1.7 MeV He ions. The backscattered particles were detected by a silicon surface barrier detector at a backscattering angle of 170 deg.

The optical properties of annealed RE implanted ZnO 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 detectors: liquid nitrogen cooled InGaAs detector for measurements in the IR region and a photomultiplier (Hamamatsu H7732-10) for the UV-visible 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 from the Hall effect measurements performed in the Van der Pauw geometry [42] on 10 mm \times 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 by e-beam evaporation of a 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



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

transformations processes in ZnO implanted with Yb and Er were studied. Fig. 1 shows the typical RBS random and aligned spectra obtained for ZnO implanted with different fluences of RE ions. The Zn signal in the RBS spectra and the signal originating from RE are separated, which enables the 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 Fig. 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 [40] for ZnO:RE system decreases as a function of increasing ion fluence. The numerically evaluated substitutional fractions of RE after subsequent implantations as well as the value of channeling minimum yield (χ_{min}) parameters [40], representing the level of the structural defects in Zn and Yb sublattice are presented in Table 1. The results of calculation indicate that for the fluencies higher than 2 \times 10^{15}/cm^2, the process of RE ions rejection to the interstitial positions is accelerated, but still, about 30% of Yb atoms remain in Zn-substitutional positions along the (0001) direction. Any significant difference in the behavior of Yb and Er ions in the ZnO matrix was not noticed. However, it is worth noting that for similar fluences of Gd-ions implanted into ZnO the lower values of $\chi_{\text{min}}(\text{Zn})$ can be found in the literature [43-44]. Such differences can be assigned to different implantation conditions, where the ZnO:Gd films were implanted with five times lower energy or at a higher temperature of the implantation process, than used in the present experiments, resulting in a lower level of structural defects formed during the implantation with the same RE ions fluences. Looking at the low energy region of the RBS/c spectra, no visible change in the aligned spectra for low fluences of RE was remarked. Starting from the fluence of 2.5×10^{14} /cm² the small double-

Table 1

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

Concentration of Yb [10 ¹⁵ at/cm ²]	χ_{min} (Zn)	χ _{min} (Yb)	f_s
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

damage peak at the top of the dechanneling background appears and grows up to the fluence equal to $1.5 \times 10^{15} / \mathrm{cm}^2$ without changing the energy position. Above the fluence of $2 \times 10^{15} / \mathrm{cm}^2$, the damage peak intensity sustains its enhancement with the maximum shifted towards lower energy (i.e. higher depths). Such results indicate that upon ion implantation to the fluence above of $1.5 \times 10^{15} / \mathrm{cm}^2$ a complicated defect structure has developed. The level of lattice damage after implantation is very similar for both investigated ions.

The *McChasy* computer code [45–46] 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 Fig. 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 they are modeled as dislocations (DIS). The 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 are shown in Fig. 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



Fig. 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.



Fig. 3. Depth distributions of defects such as a) randomly displaced atoms (RDA), b) dislocation (DIS) obtained from *McChasy* simulations.

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 the DP peak is located at about 40 nm, thus deeper than indicated by theoretical calculations using the SRIM code [39]. 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 [38]. Finally, the region between them (15-25 nm from the surface), where the low damage level is observed, is connected with the maximum nuclear energy loss R_{pd} calculated by the 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 [47]. Both RDA and DIS distributions are increasing as a function of ion fluences, but even after heavy-ion bombardment with fluences up to 1×10^{16} /cm², which corresponds to about 100 dpa (displacement per atom = number of times that an atom



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

is displaced for a given fluence) the amorphous level was not achieved. Moreover, the DIS defects are also created deeper (beyond the ion range) and, for fluences above $1.5 \times 10^{15}/\text{cm}^2$, the step-shift of DIS distributions to a higher depth 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 only in the (0001) direction. The latest papers show that the defect accumulation process for other crystallographic directions occurs differently [48–49].

The maxima of RDA and DIS distributions form the defects accumulation curves presented in Fig. 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 [47,50–52]. In the case of ZnO-ALD films, a 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) [50]. As can be seen in Fig. 4, the accumulation rate of both kinds of defects is very low in the low fluence region. Generally, the dynamic heating during the implantation 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 [47,52]. That kind of disorder (perpendicular to the c-axis) cannot be observed in the RBS/ c spectra measured along the (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 10¹⁴/cm² 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 10¹⁵/cm², 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 a

fluence of about 1.5×10^{15} /cm², 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 [52]. Such a new form of defects is resistant to thermal annealing [25]. Any significant difference has not been noticed in the accumulation processes of Yb and Er ions.

3.2. Optical analysis

The defects produced during the ion implantation process quench most of the luminescence from the ZnO film, and RE-dopants in asimplanted ZnO are optically inactive. Therefore, annealing is needed for structure recovery and dopant activation. The thermal treatment leads to the recovery of the crystal lattice damage caused by RE implanted into ZnO, but it is associated with a simultaneous process of RE diffusion and agglomeration on the surface of the layer due to the low solubility limit [24]. Thus, the selected parameters of thermal annealing (RTA 10 min, 800 °C, O₂ atmosphere) are a tradeoff between the perfect recovery of the crystal and a stable impurity depth profile [24–25]. It is worth noting that the annealing in such conditions completely removes lattice damage from the near-surface region of ZnO [38].

In order to investigate the effect of RE-concentration inside ZnO on the PL emission intensity, the photoluminescence measurements for REion implanted-annealed ZnO layer (hereafter called ZnO:RE system), were performed at room temperature for both studied ions. The PL spectra in 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) of ZnO:Yb layer are shown in Fig. 5. For comparison, the PL results obtained for undoped ZnO and after 10 min RTA are added. For undoped ZnO (Fig. 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 the maximum at 520 nm, called deep-level emission (DLE) is due to native defects excitation. As can be seen in Fig. 5a, the annealing process enhances mainly defect luminescence and weakening of the NBE. As was reported before, the green luminescence in undoped ZnO is commonly ascribed

to zinc vacancies (Vzn) [53-54] (and oxygen vacancies, which are mostly annihilated during annealing in O₂ atmosphere [55]) as well as zinc antisites [31], red emission - to zinc vacancy clusters [55-56], while the responsibility for the yellow band is frequently assigned to excessive oxygen (O_i) [31,55]. It is worth mentioning, that experimental results on ZnO native defects published so far are not fully consistent for samples obtained by different methods and even under various growth conditions, therefore they do not offer a completely comprehensive picture of the origin of the observed DLE band. The RE implantation effectively suppresses both NBE and DLE but this luminescence returns after annealing [24,38]. Nevertheless, the observed NBE is weaker for implanted than for undoped ZnO films after annealing. However, it is interesting to note that the annealing atmospheres could significantly affect the shape of PL spectra in the visible region. As was reported by Kennedy at al. [57] annealing under UHV conditions leads to the enhancement of the edge emission in the blue spectral region, which is connected with the creation of Zn_i defects. On the other hand, oxygen annealing suppresses the blue edge emission in favor of lower-energy emission, giving a chance for moving emission towards a white color. In our case, an increase of the implantation fluence yields the stronger quenching of the NBE and DLE. Moreover, the shape of the DLE peak changes for higher RE fluences, suggesting an enhancing role of such defects as $O_{i}\ \text{and/or}\ V_{Zn}$ clusters. Besides, the influence of complexes involving these defects and the defects related to RE for doped ZnO cannot be excluded as well [58-61].

The annealing process leads also to an optical activation of Yb³⁺ and Er³⁺, which makes possible the observation of the 4f transitions characteristic for both studied 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 Yb³⁺, the main transition from the excited ²F_{5/2} to the ²F_{7/2} ground state of Yb³⁺ give a sharp peak at 980 nm (Fig. 6). Broad peaks situated between 1000 and 1040 nm correspond to the Yb³⁺ ion emission vibronic band ²F_{5/2} to the ²F_{7/2(n)}; n = 1,2,3,4) [62]. In the case of Er³⁺ the PL emission at around 1534 nm, originating from the transition from the ⁴I_{13/2} to the ⁴I_{15/2} ground state of Er³⁺ is observed (PL spectra not shown here). For both



Fig. 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 $^{\circ}$ C in an oxygen atmosphere.



Fig. 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.



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

studied ions, the emission intensity changed non-monotonically with the RE concentration in ZnO. Moreover, in Fig. 6 the small blue shift of the main peaks of RE³⁺ and the change in the vibronic band emission region for the fluences above 1.5×10^{15} /cm² can be observed, which marks the changes of the local environment or/and symmetry of the host material [63-64]. 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 Fig. 7. As can be seen, when the Yb fluence is lower than 1.5 \times 10¹⁵/cm² the PL intensity increase with the Yb content. For fluences higher than 1.5×10^{15} /cm² the PL intensity suddenly decreases, especially when the Yb content reaches 2×10^{15} / cm². Further increase of the fluence leads to a moderate increase of the PL intensity, probably because the damage level of the structure is very high and a threshold of the plastic deformation is reached. It also indirectly suggests that due to the low solubility limits of RE ions in ZnO and high mobility of atoms during annealing, not only a secondary phase of RE₂O₃ or/and other RE-related clusters may be formed [61], but optically active centers with RE 3+ ions may be created in the mosaic grain boundary region [65]. Additionally, for RE fluence higher than 2 \times 10¹⁵/cm² an agglomeration of interstitial RE ions in the optically non-active clusters form can occur. The latter supposition is consistent with the results of the electrical studies shown in the next paragraph.

It has been found that the dose-dependences described above are similar for both studied ions. However, as shown in Fig. 7, some differences between the RE dose-dependences of the PL intensity for Yb and Er are visible. In the case of erbium, the inflection point appears for a little bit lower fluence.

3.3. Electrical studies

Electrical resistivity measurements of the RE-implanted ALD–ZnO layers are consistent with 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 are presented in Fig. 8. Krajewski et al. have shown the carrier concentration of about $n \sim 10^{18}/\text{cm}^3$ for the ZnO layers implanted with Yb or Dy to the fluence of $\sim 10^{15}$ at/cm² [25]. 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 layers as a function of the Yb



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

fluence, reveal similar dependencies as reported in Ref. [25], which is also reflected in the dose-dependence of resistivity shown in Fig. 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 $1.5\,\times\,10^{15}/\text{cm}^2$ and increases gradually for 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 1.5×10^{15} RE ions/cm² 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 [38]. 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 [24,38]. Interstitial RE is in 3+ valence state, thus interstitial RE³⁺ may be considered as a donor-type defect. The resistivity enhancement observed for fluences higher than 1.5×10^{15} /cm² suggests an agglomeration of interstitial RE ions, which may lead to deactivation of a part of RE donors. Moreover, the PL spectra measured in the visible region and obtained from heavily implanted ZnO suggest the increase of the concentration of some acceptors' defects such as Oi and/or VZn as well, which may cause the compensation of free carriers, thus keeping the charge balance in the system and additionally increase the layer resistivity above the fluence of 1.5×10^{15} /cm² with the further tendency to saturate. Such a hypothesis may also be found in the literature, describing similar studies [28,31,65].

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 was 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 shown, that the defect accumulation in RE ion-implanted ZnO film 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 2×10^{14} /cm²) does not cause the damage in the (0001) direction. However, as demonstrated by our previous works, an increase of stress along the *c*-direction with increasing ions fluences can be expected. Consequently, interstitial atoms, small point clusters and dislocation loops in other than the (0001) direction are formed. When the critical value of the stress has been achieved, a 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. The nature of these clusters needs to be further studied. For RE implanted ZnO-ALD films, the threshold of such process (maximum of the stress) was evaluated for the ion fluence about 1.5×10^{15} /cm², which corresponds to the values of ~8 dpa. This process seems to be completely finished for the fluencies above 5×10^{15} /cm². After implantation, a part of implanted RE atoms is located at the substitutional lattice positions along the (0001) direction. However, a substitutional fraction of RE ions decreases as a function of increasing ion fluence. Any significant difference in the accumulation processes and behavior of Yb and Er ions in the ZnO matrix was not noticed.

An increase of stress for higher RE fluence also contributes to an enhanced packing of RE centers. 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 RE³⁺ luminescence. Interestingly, above the plastic transformation threshold the PL intensity from RE³⁺ increases again as a function of ion fluencies with a tendency to saturate. It can be associated with the precipitations and agglomeration of RE in the ZnO lattice which is accompanied by the creation of various defects clusters as observed in the PL response in the visible region. Because of that, the similar luminance efficiency was obtained for the fluencies of 1×10^{15} and 5×10^{15} /cm². These changes are consistent with the characteristic course of resistivity versus ion fluence dependence, because the agglomeration of interstitial RE may lead to the deactivation of a part of RE ions.

Author contribution

Renata Ratajczak: Conceptualization, Methodology, Funding acquisition, Project administration, RBS and PL Investigation and Visualization, Writing - Original Draft, Writing - Review & Editing. Cyprian Mieszczynski: Software, Validation, Formal analysis. Sławomir Prucnal: Supervisor of PL studies, Formal analysis. Tomasz A. Krajewski: Supervisor of Hall effect studies, Hall Investigation and Visualization of Hall results, Formal analysis, Writing - Review & Editing. Elżbieta Guziewicz: Resources, Supervisor of ALD growth, Writing - Review & Editing. Wojciech Wozniak: Resources, Formal analysis of ALD growth processes. Krzysztof Kopalko: Resources, Formal analysis of RTA processes. Rene Heller: Supervisor of RBS/c studies. Shavkat Akhmadaliev: Resources, Supervisor of implantation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research was carried out under the co-financed international project supported by the Polish Ministry of Science and Higher Education (3846/HZDR/2018/0) and Helmholtz-Zentrum Dresden-Rossendorf (17000941-ST) and the project of National Centre for Research and Development (PBS2/A5/34/2013)).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.146421.

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