Optical Response of Epitaxial ZnO Films grown by ALD and co-implanted with Dy and Yb

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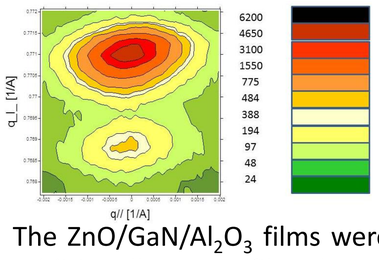
Motivation

Rare Earth (RE) implanted wide-band-gap semiconductors like ZnO or GaN have been investigated for a range of possible optoelectronic applications. The ZnO excitonic violet-blue emission combined with visible emission from RE has potential to be applied in phosphors and other opto-electronic devices. Ion implantation is a convenient method for introduction of RE ions into the crystal because RE concentration and depth profile can be easily controlled.

Our previous investigations on ZnO doped with Yb, Pr and Dy ions show that room temperature (RT) photoluminescence (PL) spectra of annealed ZnO_ALD:RE films do not show any sharp lines, but the PL response obviously depends on a type of RE ion. Color temperature of ZnO:Yb films was found to be close to 4000K, while for ZnO:Dy the correlated color temperature was 2400K. Co-doping with Dy and Yb ions was found to be a prospective way to tune the color temperature between 2400K and 4000K as well as to move the colorimetric coordinates towards the Plankian locus.

Experimental

Epitaxial ZnO films were grown by Atomic Layer Deposition (ALD) which is a relatively inexpensive deposition method with great industrial potential. The ~900 nm thick ZnO films were deposited with diethylzinc and water precursors at 300°C on a GaN/Al_2O_3 template.



The ZnO/GaN/Al_2O_3 films are grown with the *c* axis perpendicular to the surface (only two XRD reflections from 002 and 004 planes were observed). The FWHM of the 002 reflection is 158" (~0.04°), the same value was obtained for the GaN substrate.

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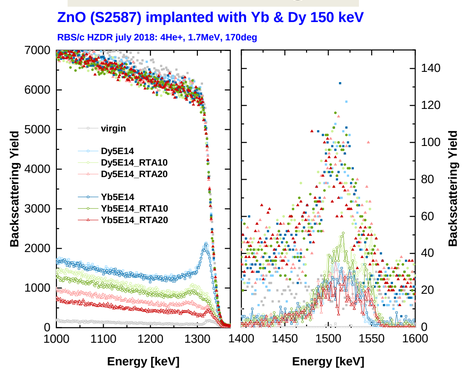
The ZnO/GaN/Al_2O_3 films were implanted with Yb and Dy ions to the fluence of $5 \cdot 10^{14}/cm^2$. Additionally, some films have been co-implanted with Yb and Dy ions to the same fluence each.

In order to recover the ZnO crystal lattice and activate dopants, the post-growth Rapid Thermal Processing (RTP) in oxygen atmosphere at 800°C for 10 min. has been performed after ion implantation.

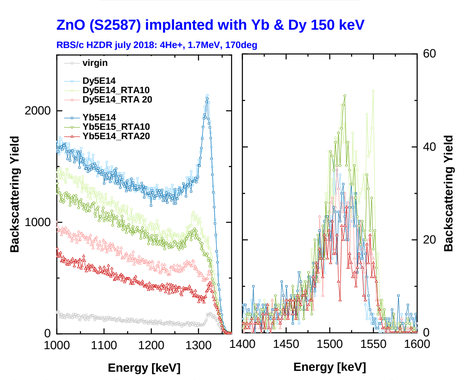
The Channeling Rutherford Backscattering Spectrometry (RBS/c) has been used to evaluate the location of RE ions and it was correlated with RT photoluminescence.

Implantation with Yb or Dy ions

RBS – random & aligned

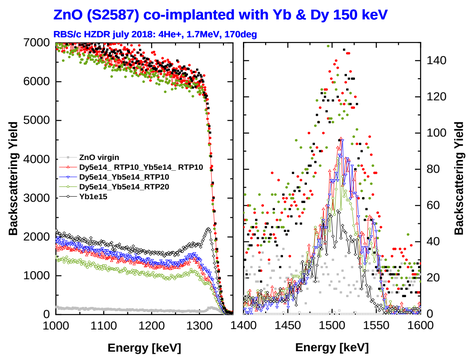


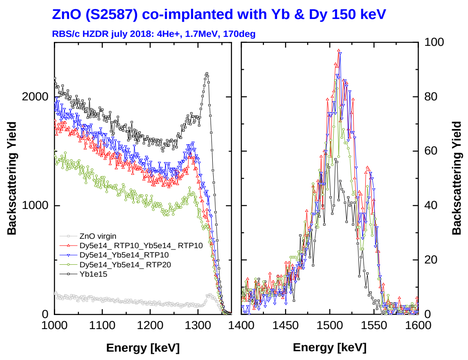
RBS – aligned spectra



Energy range 1000-1400 keV: It has been found that damage built-up after implantation is similar for Dy and Yb ions. However, after the same RTP annealing (O_2, 800°C, 10 or 20 min.), the recovery of the ZnO crystal lattice is more efficient in case of ZnO:Yb than for ZnO:Dy. **Energy range 1400-1600 keV:** The RBS spectra show that Dy ions are more mobile than Yb ions that results in much stronger Dy out-diffusion and in higher amount of Dy-ions at the sample surface in comparison with Yb ions. The longer annealing is conducive to the ordering of the dopant ions in the ZnO matrix.

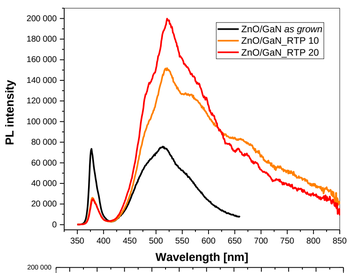
Co-implantation with Yb & Dy ions



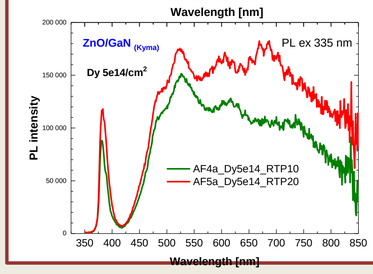


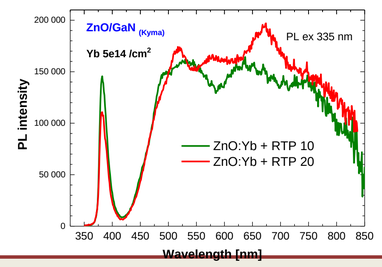
Energy range 1000-1400 keV: It has been found that, in case of Yb and Dy co-implantation, better recovery of the ZnO crystal lattice is achieved when one 20 min. annealing process is applied instead of two RTP processes, each after one implantation step (Dy or Yb). **Energy range 1400-1600 keV:** The RBS spectra show that similar out-diffusion processes of RE ions are observed after the 10 min. and 20 min. RTP. However, it seems that one long-step annealing is conducive to the ordering of the dopant ions in the ZnO matrix.

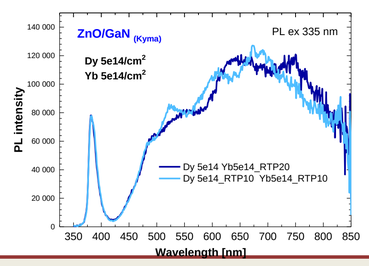
Room temperature photoluminescence



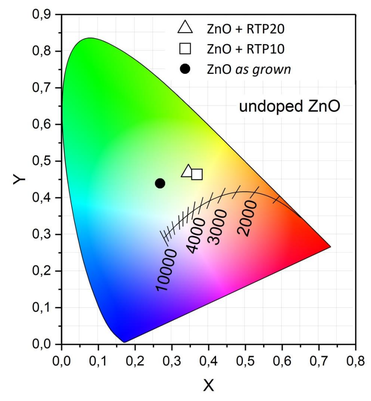
RT PL spectra of *as grown* epitaxial ZnO/GaN films show blue band-edge PL of excitonic origin together with green PL band centered @ 510-520 nm. Although the ratio between both PL bands can be tuned by annealing, the colorimetric parameters are placed far from the Plankian locus. It is because of a very weak PL in the red region. Implantation by Dy or Yb ions result in much higher PL in the red region of the spectra.



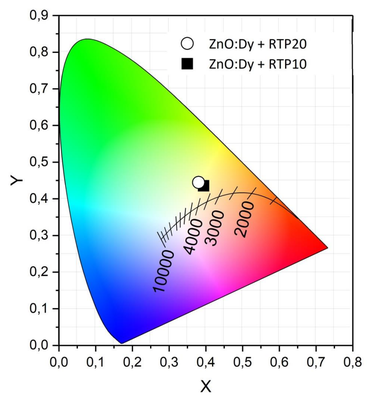


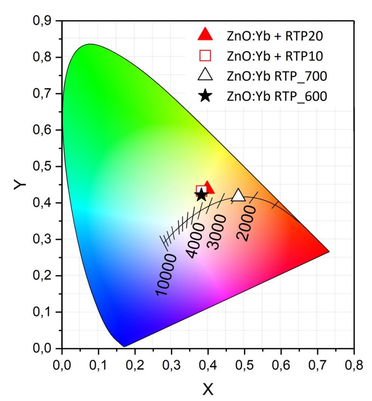


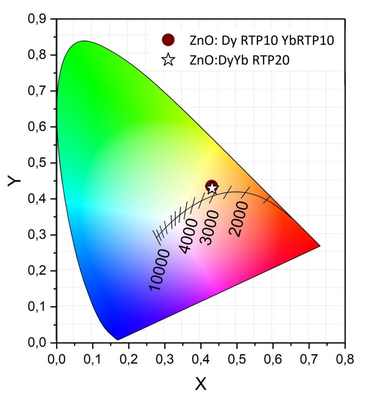
Colorimetric study



Colorimetric analysis of the RT PL spectra show that ZnO-ALD films, both *as grown* and annealed, provide light emission with color coordinates far from the black-body emission, which means that it is not white color light. Single doping with Dy or Yb ions considerably moves the light emission towards the white emission. Applied annealing time (10 or 20 min.) seems do not have noticeable influence on the color of the light. Sequential implantation with Dy and Yb ions allows achieving the optical output very close to the Plankian locus with correlated color temperature of 3200K. Such color temperature is highly appreciated for indoor light applications.







The CIE (x,y) chromaticity diagram showing coordinates of ZnO:Yb, ZnO:Dy and ZnO:(Yb,Dy) films.

Colorimetric parameters	ZnO-ALD			ZnO:Dy		ZnO:Yb		ZnO:(Yb,Dy)	
	as grown	RTP10	RTP20	RTP10	RTP20	RTP10	RTP20	2xRTP10	RTP20
X (red)	0,2680	0,3683	0,3451	0,3938	0,3803	0,3827	0,3977	0,4300	0,4312
Y (green)	0,4390	0,4637	0,4686	0,4353	0,4444	0,4326	0,4376	0,4351	0,4293
Z (blue)	0,2930	0,1680	0,1863	0,1709	0,1753	0,1847	0,1647	0,1349	0,1395
T_c	N/A	N/A	N/A	~4000K	N/A	~4000K	~3700K	3200K	3200K

Conclusions

- **It has been found that damage built-up after implantation is similar for Dy and Yb ions, but in case of ZnO:Yb crystal structure recovery is more efficient than for ZnO:Dy.**
- **Co-implantation with Dy and Yb results in lowering of out-diffusion process of Dy ions.**
- **One longer RTP annealing step (20 min.) is beneficial for ZnO crystal lattice recovery.**
- **Colorimetric analysis of the RT PL spectra show that co-implantation with Dy and Yb ions allows moving the optical response of ZnO:RE films towards the white color light with correlated color temperature 3200K, which is appropriate for indoor lighting.**

References:

[1] E. Guziewicz, S. Kobyakov, R. Ratajczak, W. Wozniak, A. Kaminska, *Phys. Stat. Solidi B,* **2020**, 1900513 (1-7)

[2] R. Ratajczak, E. Guziewicz, S. Prucnal, G. , R. Böttger, R. Heller, C. Mieszczynski, W. Wozniak, A. Turos, *Phys. Stat. Sol. A,* **2018,** 1700889 (1-7)

[3] E. Guziewicz, R. Ratajczak, M. Stachowicz, D. Snigurenko, T.A. Krajewski, C. Mieszczynski, K. Mazur, B.S. Witkowski, P. Dluzewski, K. Morawiec, A. Turos, *Thin Solid Films*, 643, **2017**, 7-15.

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