Wide-Bandgap Oxides implanted with Rare-Earth: Study of Crystal Structure Damage and Recovery

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Motivation

Rare earths (RE) are important for the optical tuning of wide bandgap oxides (WBO) as Ga_2O_3 or ZnO because Ga_2O_3:RE or ZnO:RE show narrow emission lines in the visible, ultra-violet and in some cases in the infra-red region. This aspect of WBO:RE makes them stand out for prospective applications in optoelectronics. Ion implantation is an attractive method to introduce RE into the crystal lattice because of precise control of dopant dose, but it creates the lattice damage, which may cause RE to be optically inactive. Post-implantation thermal treatment of the implanted material at the appropriate temperature and environment can recover the lattice damage and activate the RE emission [1, 2]. In this research work, we aim to investigate and compare the post-implantation lattice damage of two matrices of WBO materials, β-Ga_2O_3 and ZnO, implanted with RE and recovery of the crystal structure after annealing.

Experiment and Characterization

Material

Commercially available single crystal Ga_2O_3 and epitaxial ZnO films grown by Atomic Layer Deposition (ALD) were implanted with RE. The epitaxial ZnO films (~2µm thick) were deposited at 300°C on GaN/Al_2O_3 substrate by using diethyl zinc and deionized water precursor.

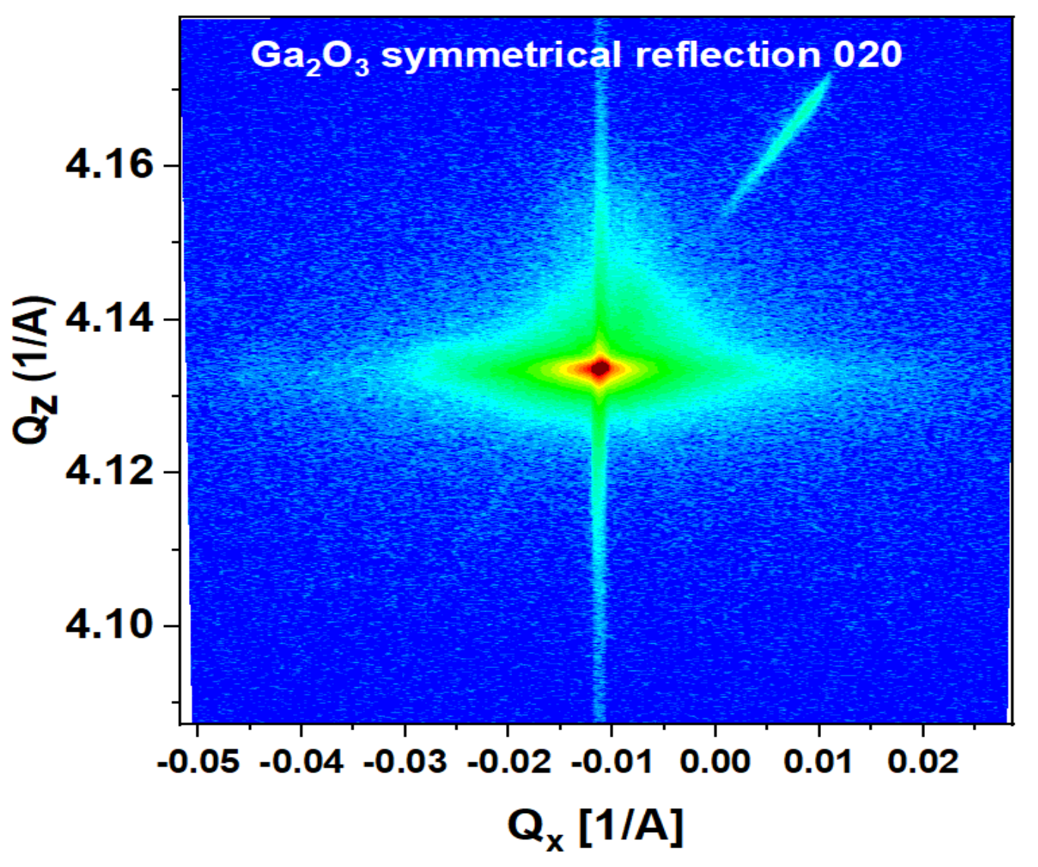
Implantation

Both materials were implanted with Sm or Eu ions to a fluence of 5×10^{14}, 1×10^{15} and 3×10^{15} atoms/cm^2. In order to recover the lattice damage created by implantation, implanted β-Ga_2O_3 was Rapid Thermal Annealed (RTA) in Ar and epitaxial ZnO films were annealed in O_2 at 800°C.

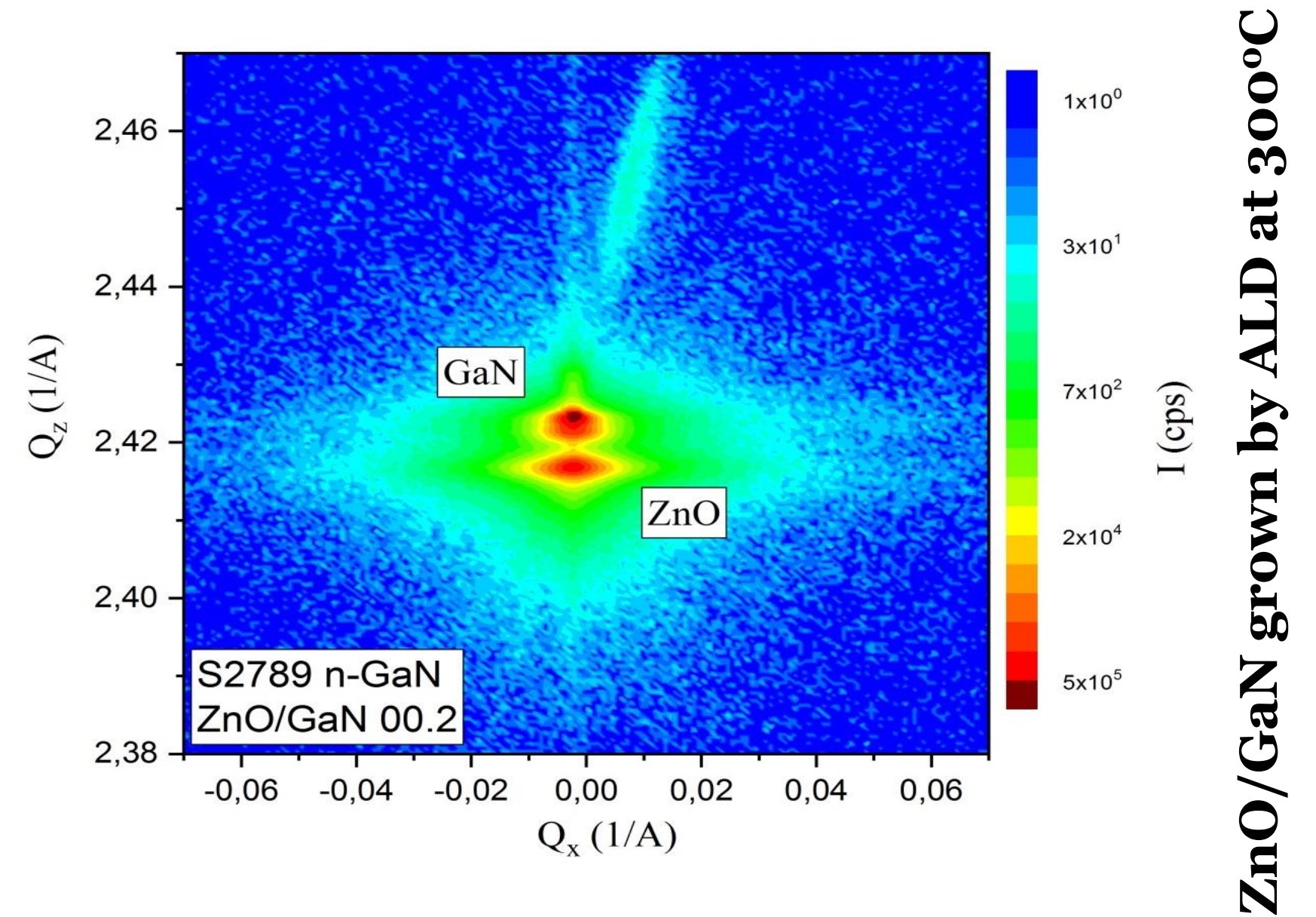
Analysis

Channeling Rutherford Backscattering Spectrometry (RBS/c) has been used to evaluate the structural damage after implantation, recovery of the lattice after RTA and lattice site location of RE. SIMNRA , a simulation code , was used to find out the RE concentration and its depth profile in the matrix from RBS random spectra. McChasy code based on Monte Carlo simulations was used to quantify the damage depth profile (Randomly Displaced Atoms RDA and Dislocations DIS) of the RBS spectra in the channeling mode. Low Temperature Photoluminesence (LTPL) of implanted samples was performed to detect the optical activation of RE.

HR XRD (β-Ga_2O_3 and ZnO)



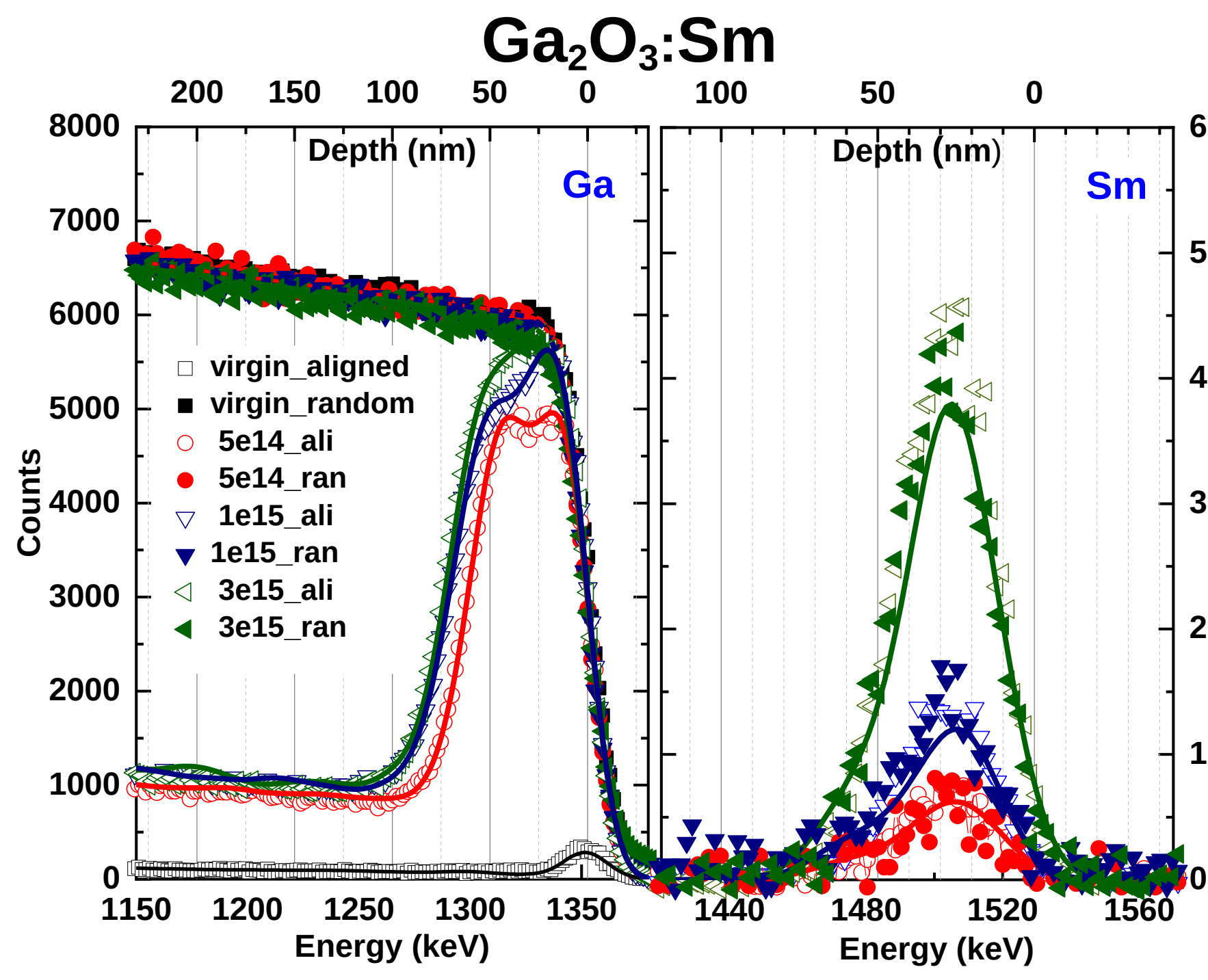
Reciprocal Space Maps (RSM) of the symmetric 020 XRD peak of β-Ga_2O_3



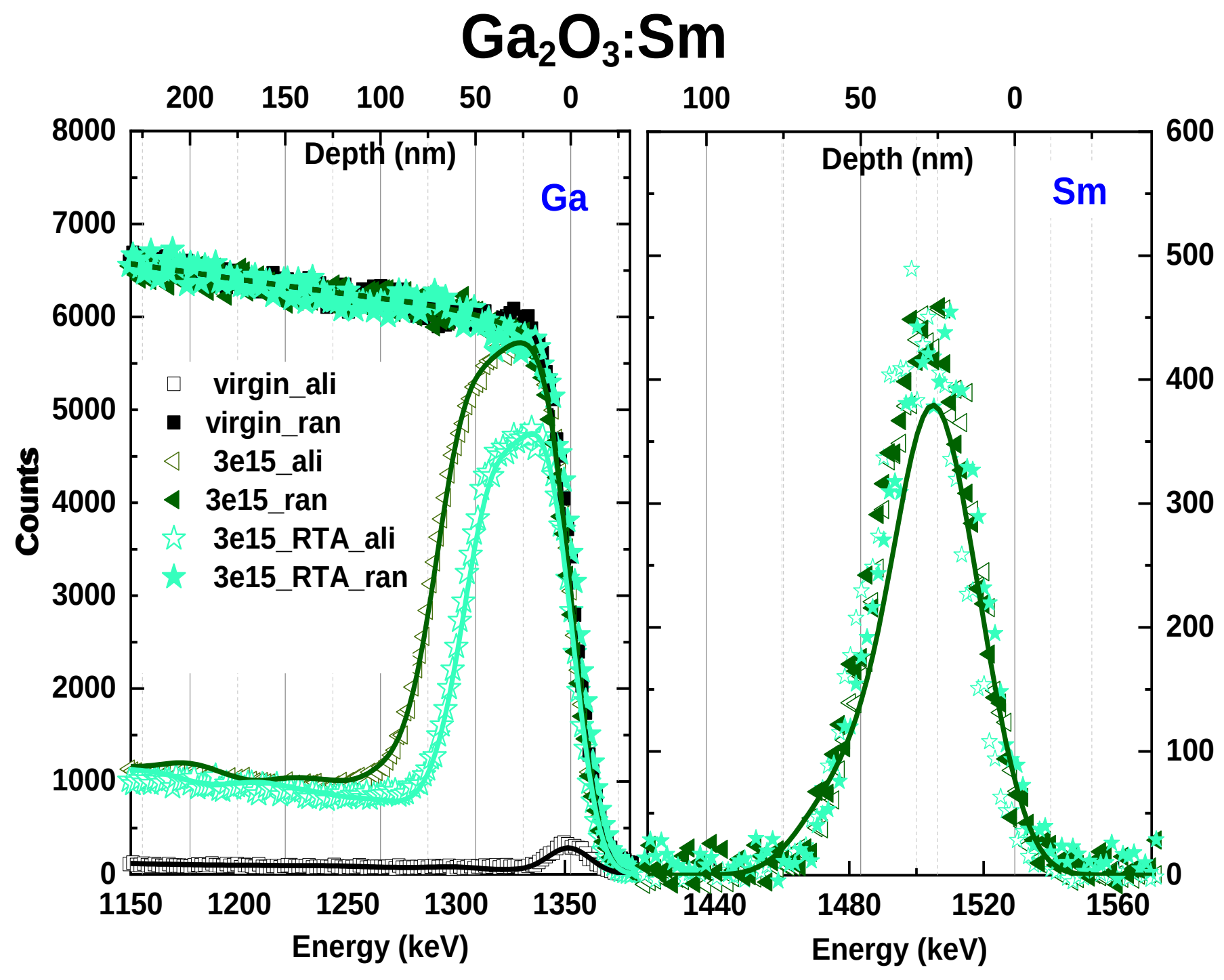
Reciprocal Space Maps (RSM)of the symmetric 00.2 XRD peak of ZnO

- In the reciprocal space maps, the sharp and well defined XRD signal coming from β-Ga_2O_3 and ZnO/GaN shows the good quality of both materials.

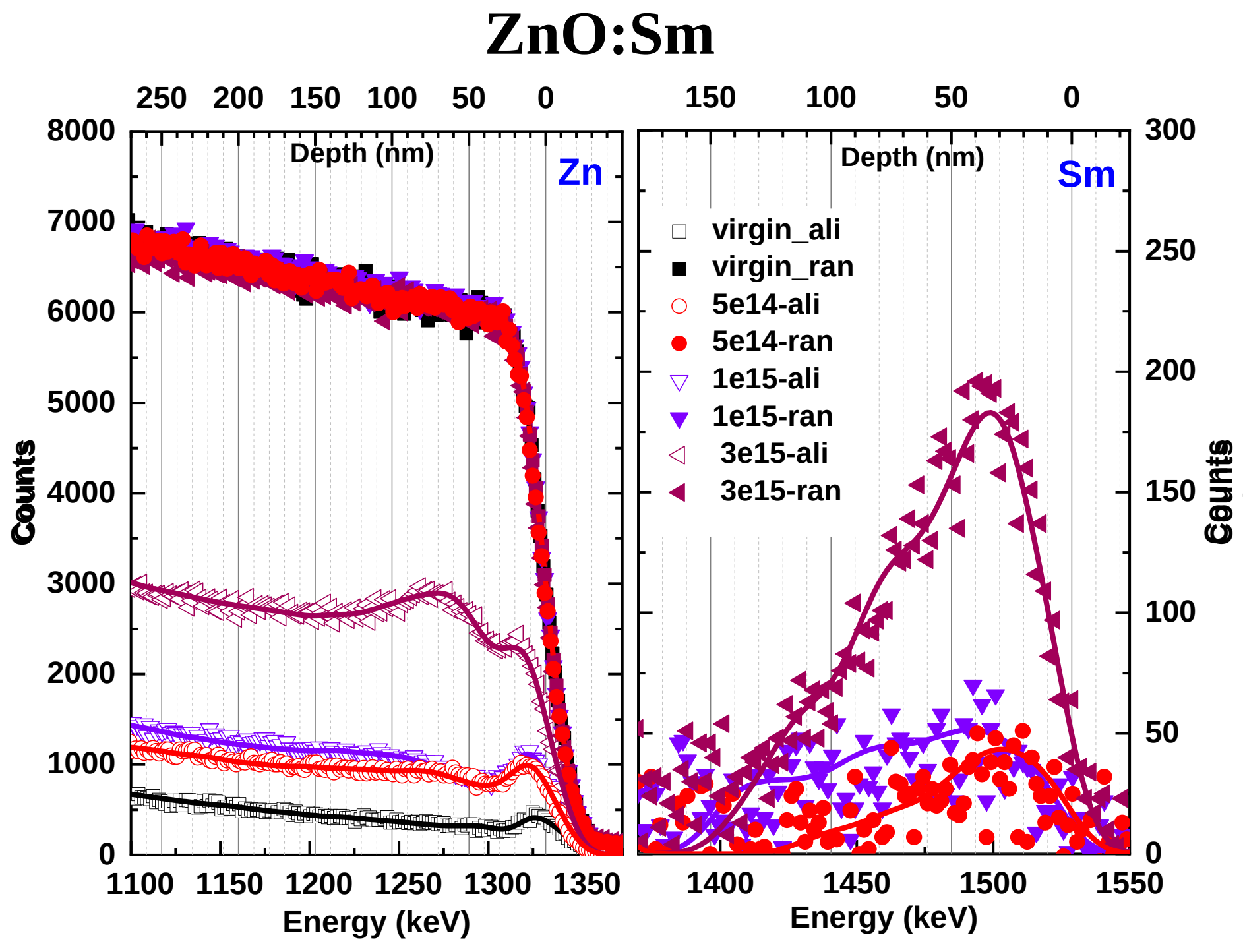
Rutherford Backscattering Spectrometry (RBS/c)



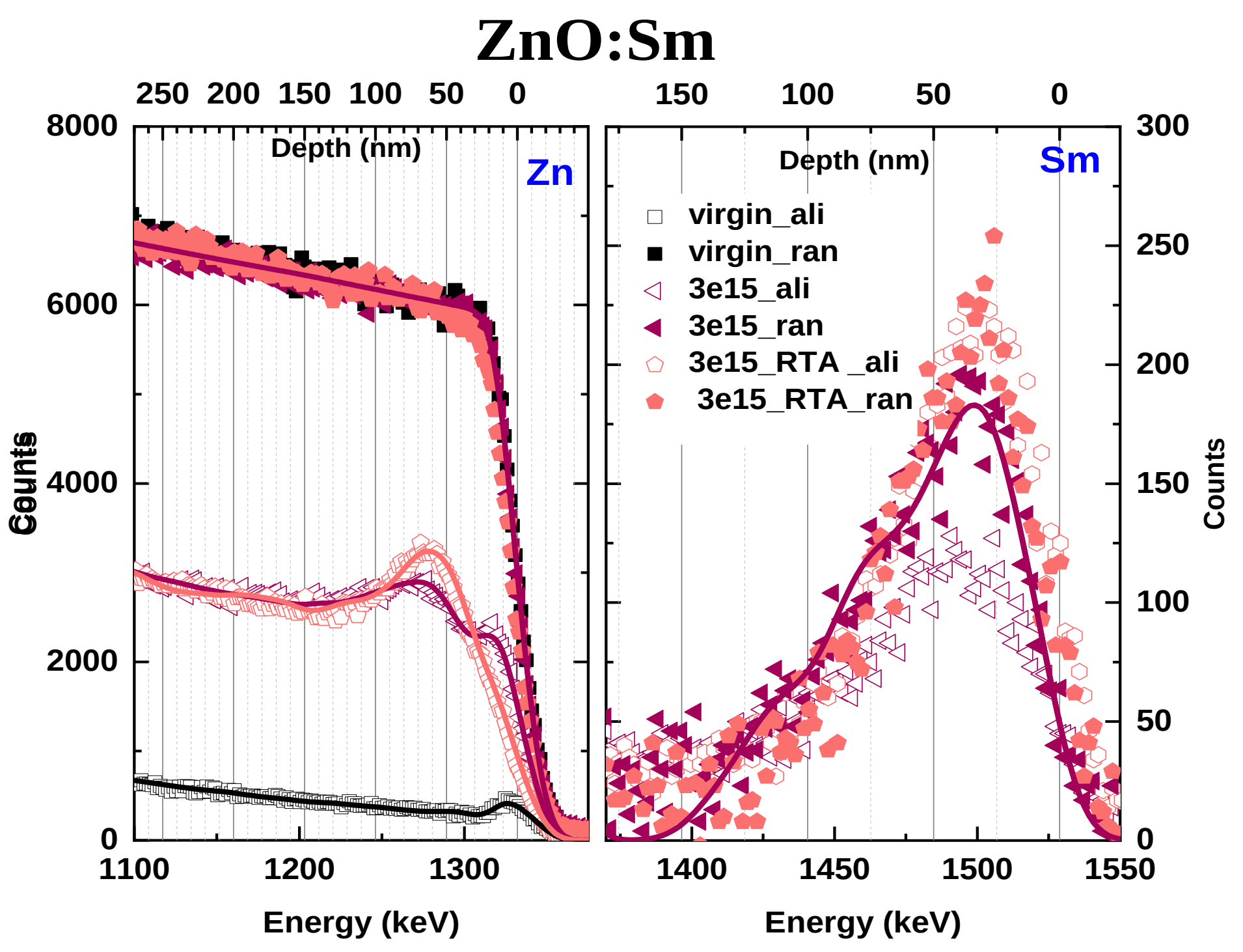
Random and aligned RBS spectra for β-Ga_2O_3 implanted with Sm. The solid lines show the results of MC simulations of the spectra.



Random and aligned RBS spectra for β-Ga_2O_3 implanted with Sm annealed in Ar at 800°C for 30 sec. The solid lines show the results of MC simulations of the spectra.

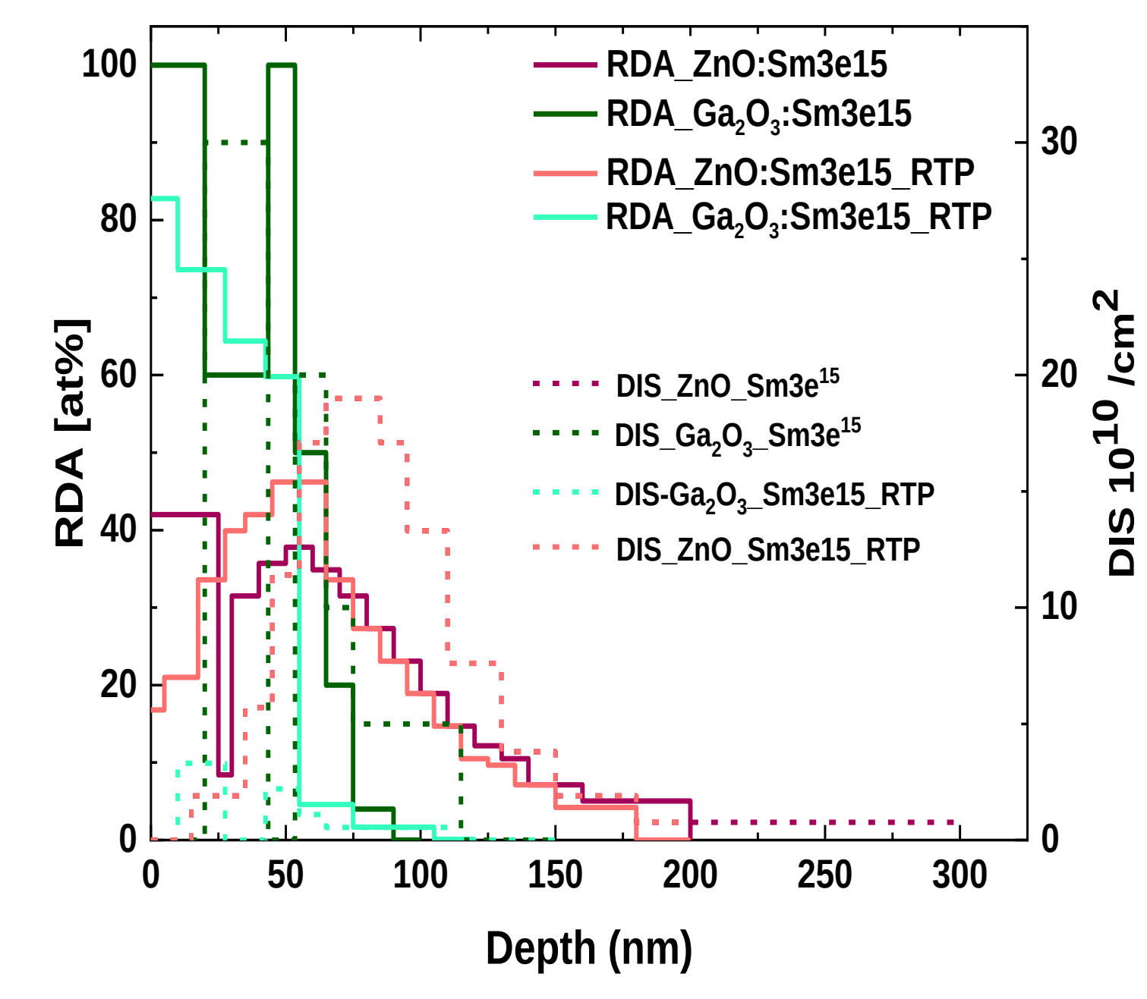


Random and aligned RBS spectra for ZnO implanted with Sm. The solid lines show the results of MC simulations of the spectra.

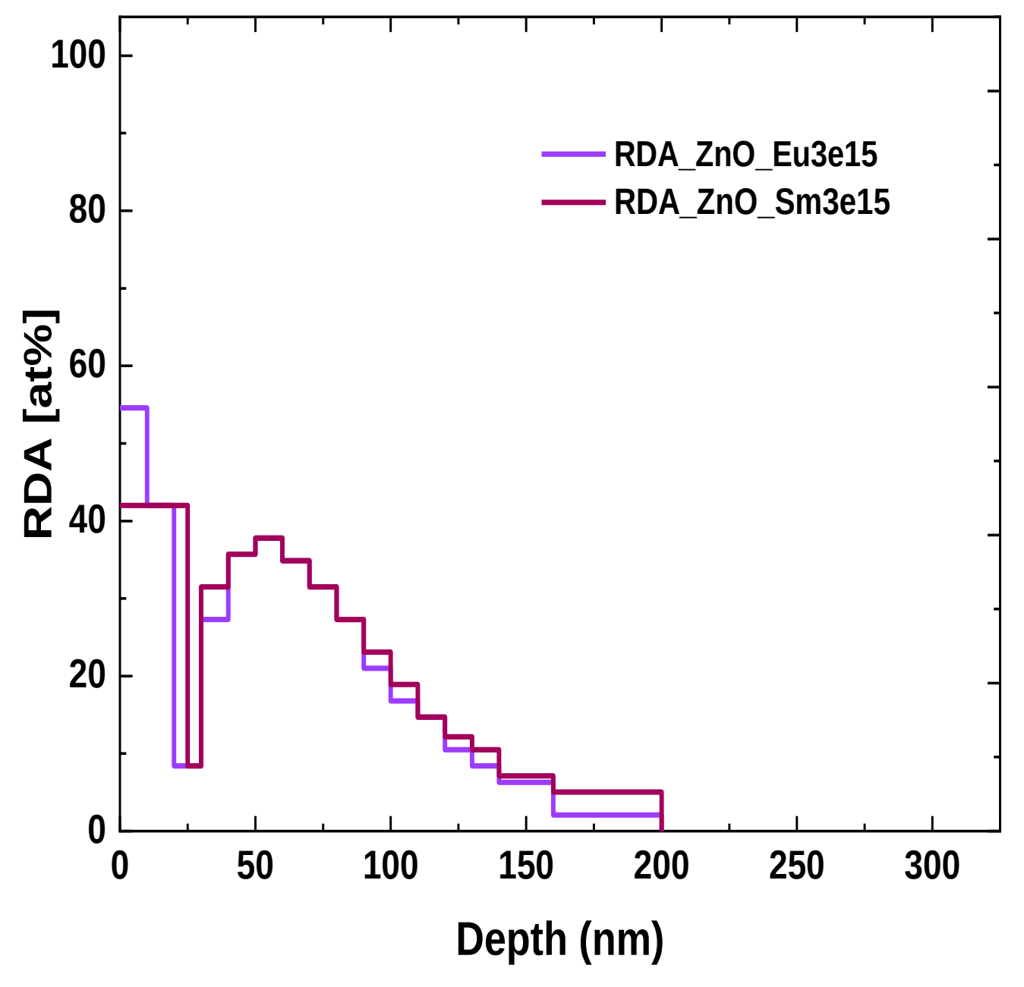


Random and aligned RBS spectra for ZnO implanted with Sm annealed in O_2 at 800°C for 10 min. . The solid lines show the results of MC simulations of the spectra.

Defects Distributions by McChasy



Distribution of RDA and DIS defects for imlanted β-Ga_2O_3 + ZnO obtained by McChasy Simulations



Distribution of RDA defects for ZnO:Eu and ZnO:Sm obtained by McChasy Simulations

	Fluence (at/cm^2)	Conc. of RE (10^{15}at/cm^2)	χ_{min} (Ga)	χ_{min} (Zn)	χ_{min} (Sm)	f_s
β-Ga_2O_3:Sm	virgin	-	1.4	-	-	
	5e14 RTP_Ar	0.44 -	81.9 67.5	-	100 100	0 0
	1e15 RTP_Ar	0.96 -	89.6 78.6	-	100 100	0 0
	3e15 RTP_Ar	2.76 -	101.8 80.1	-	100 100	0 0
ZnO:Sm	virgin	-	-	5.3	-	-
	5e14 RTP_O_2	0.61 -	-	14.2 7.1	57 75	44 26
	1e15 RTP_O_2	1.00 -	-	14.7 11.5	61 100	40 0
	3e15 RTP_O_2	2.86 -	-	44.2 48.4	56 100	53 0

Conc. of RE calculated by SIMNRA and substitutional fraction (f_s) calculated by RBS/c spectra

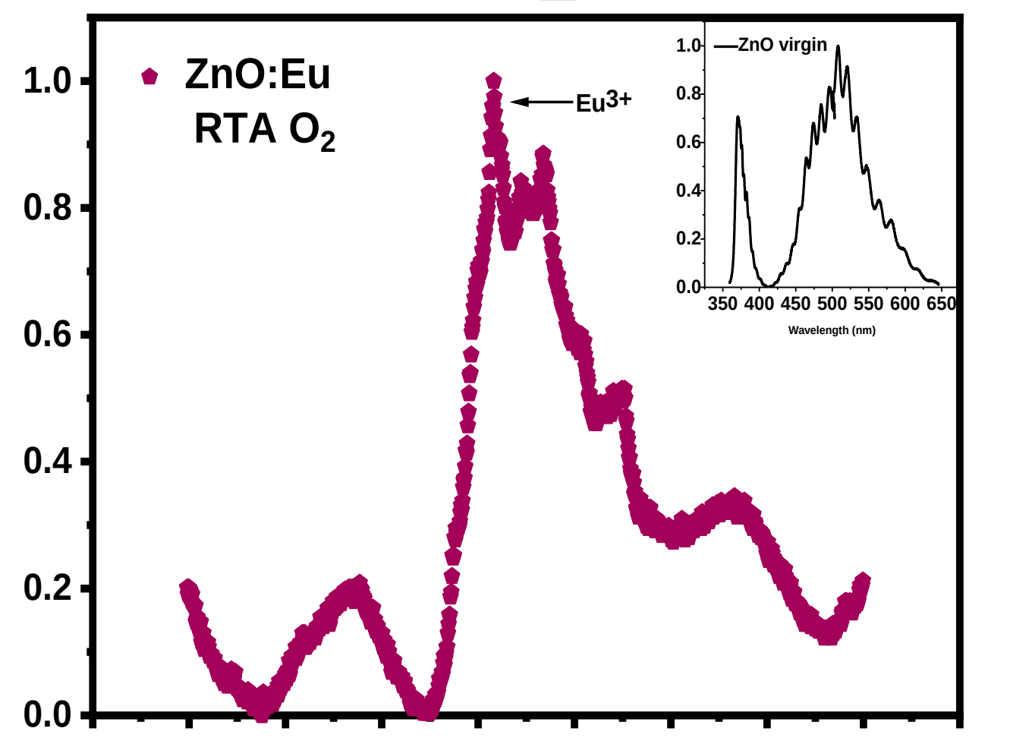
β-Ga_2O_3 implanted with Sm

- Atypical damage peak near the surface (IP) shows ~**100 %** of **RDA** which continues till **~20nm**. Characteristic for the implanted materials damage at depth, located close to the projected range of implanted ions, extends between 20-80nm for RDA. **DIS** type of defects are shifted up to **~110nm**
- Both RDA and DIS decreased after annealing in Ar.
- Substitutional fraction f_s is zero for all the Ga_2O_3 samples → impurity atoms at interstitial position.

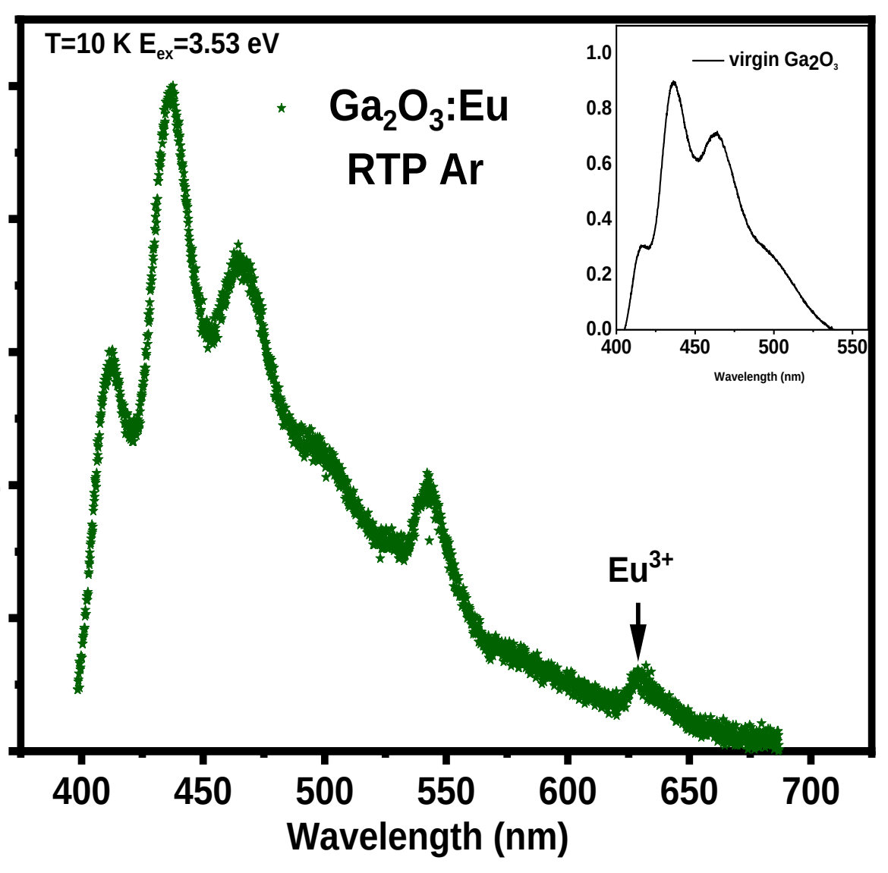
ZnO implanted with Sm and Eu

- The peak near the surface damage extends until ~25 nm showing ~**41%** of **RDA**, small depleted region and bulk peak from ~30nm to ~150 nm.
- After annealing , the surface peak has disappeared, but RDA in bulk peak has increased, which shows diffusion of defects towards the surface.
- f_s → impurity atoms partially are located in substitutions position after implantation, and they moved to interstitial position after annealing
- Depth defects distributions obtained by McChasy for ZnO implanted with Eu are identical to ZnO implanted with Sm.

Low Temperature Photoluminescence



LT PL spectra for ZnO and ZnO:Eu annealed in O2 at 800 °C for 10 min



LT PL spectra for β-Ga_2O_3 and β-Ga_2O_3:Eu annealed in Ar at 800 °C for 30 sec

- ZnO Sharp NBE peak at 375nm and DLE centered around 510 nm
- ZnO:Eu shows the Eu peak at red spectral region closer to 600 nm
- β-Ga_2O_3 shows emission lines in visible and ultraviolet region
- β-Ga_2O_3 shows the Eu peak around 625 nm showing optical activation of RE after annealing

Conclusions

- Rutherford backscattering spectrometry in channeling mode was used to assess the crystal quality, lattice site location of RE, post-implantation damage and post annealing recovery of the crystal structure of β-Ga_2O_3 and ZnO implanted with RE.
- For β-Ga_2O_3 , annealing in the Ar atmosphere at 800°C for 30 sec and for ZnO implanted with Sm, annealing in O_2 at 800 °C for 10 mins reduces damage near the surface indicating the removal of defects on IP region.
- According to our findings, β-Ga_2O_3 is less radiation resistant as compared to ZnO. Calculation of substitutional fraction shows that for the same fluence of dopant ion, impurity atoms are located in interstitial sites, but for ZnO, impurity atoms are mostly in substitutional positions, and move to interstitial sites after annealing.
- RBS results for ZnO implanted with Sm and Eu illustrate the same defects distribution and same behavior of both ions after implantation. Based on that, we assume that RBS/c spectra for β-Ga_2O_3 with Eu could be similar to spectra obtained for Sm implanted samples and the same annealing conditions could activate RE.
- We observed activation of the Eu related emission both in ZnO and Ga_2O_3 matrices after performed RTP annealing, however the luminescence response was not very high, so annealing conditions should be optimized

References:

[1] K. Lorenz et al., Proc. of SPIE 8987 **(2014)**
[2] R. Ratajczak et al., Appl. Surf. Sci. 521 **(2020)**

Acknowledgement

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