Cathodoluminescence Study of Acceptor- and Donor-related Emission of ZnO or ZnO:N Films Annealed Under O_2 or N_2 Atmosphere

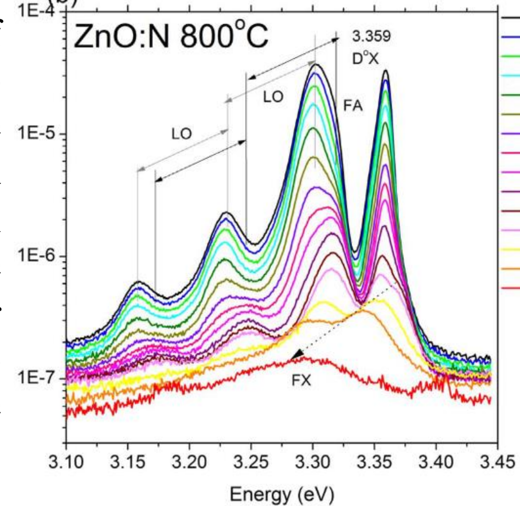
Sushma Mishra, Bartłomiej S. Witkowski, Rafał Jakieła , Zeinab Khosravizadeh, Wojciech Paszkowicz, Adrian Sulich, Wojciech Woźniak, Elżbieta Guziewicz

Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, PL-02 668 Warsaw, Poland

presenting author e-mail: shmbpj@ifpan.edu.pl

Motivation

Worldwide efforts are being made to better understand the activation of acceptor states in ZnO, with the goal of achieving long-desired *p*-type conductivity. Annealing study was performed to better understand the variation in acceptor- or donor-related emission in polycrystalline ZnO and ZnO:N, because annealing at different temperature and atmosphere can simultaneously activate acceptors and decrease structural disorder. We compared 1.5 micron thick ZnO and ZnO:N films deposited by Atomic Layer Deposition (ALD) on HR-Si (100) under O-rich conditions (100°C) and post-growth annealed at 6 different temperatures 400-900°C under N_2/O_2 atm. The intensity of acceptor-related and donor-related cathodoluminescence (CL), impurities concentration, structure of the films and RT-Hall have been investigated after different type of annealing. The experiment was carried out for N concentrations ranging from 10^{17} to 10^{19} at/cm^3.

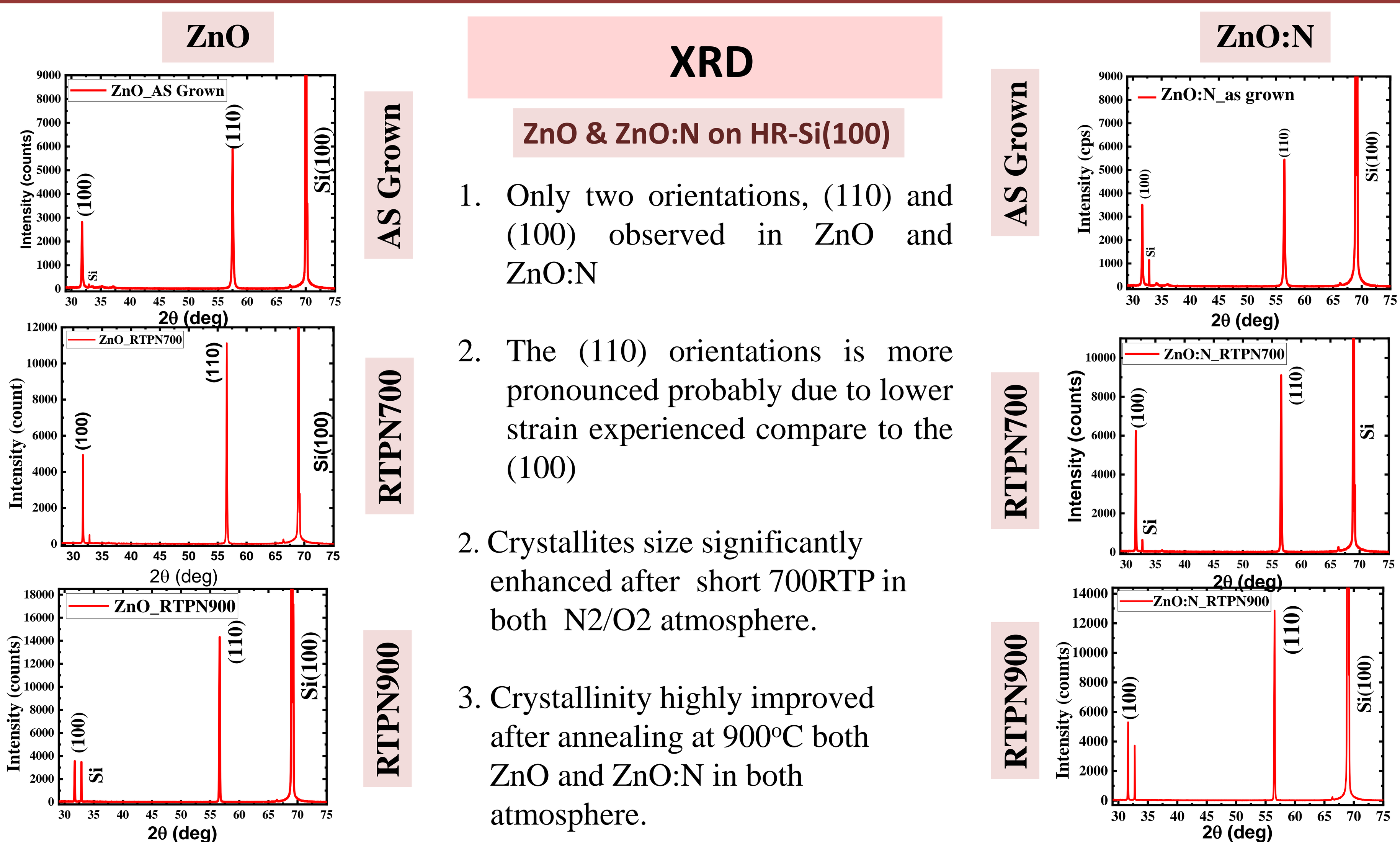


Ref: Przezdziecka, Guziewicz & Witkowski (2018) Journal of Luminescence, 198, 68-76.

Experimental

1. Polycrystalline ~1.5μ thick ZnO/Si(HR) and ZnO:N/Si(HR) films were deposited at 100°C (O-rich conditions) by ALD using the same deposition parameters
2. Two types of substrates, HR-Si(100), 5000Ωcm (324μ) and 10000 Ω cm(525 μ) used for ZnO and ZnO:N deposition
3. RTA post-growth annealing at six temperature (400 – 900°C) under N_2/O_2 atm. for 5 min.
4. Measurements:
   XRD → orientation and size of crystallites
   SIMS → H and C concentrations
   LT-CL → intensity of acceptor/donor related emission in ZnO and ZnO:N
   RT-Hall → electrical characteristic of the films (carrier concentration, resistivity and mobility)

XRD



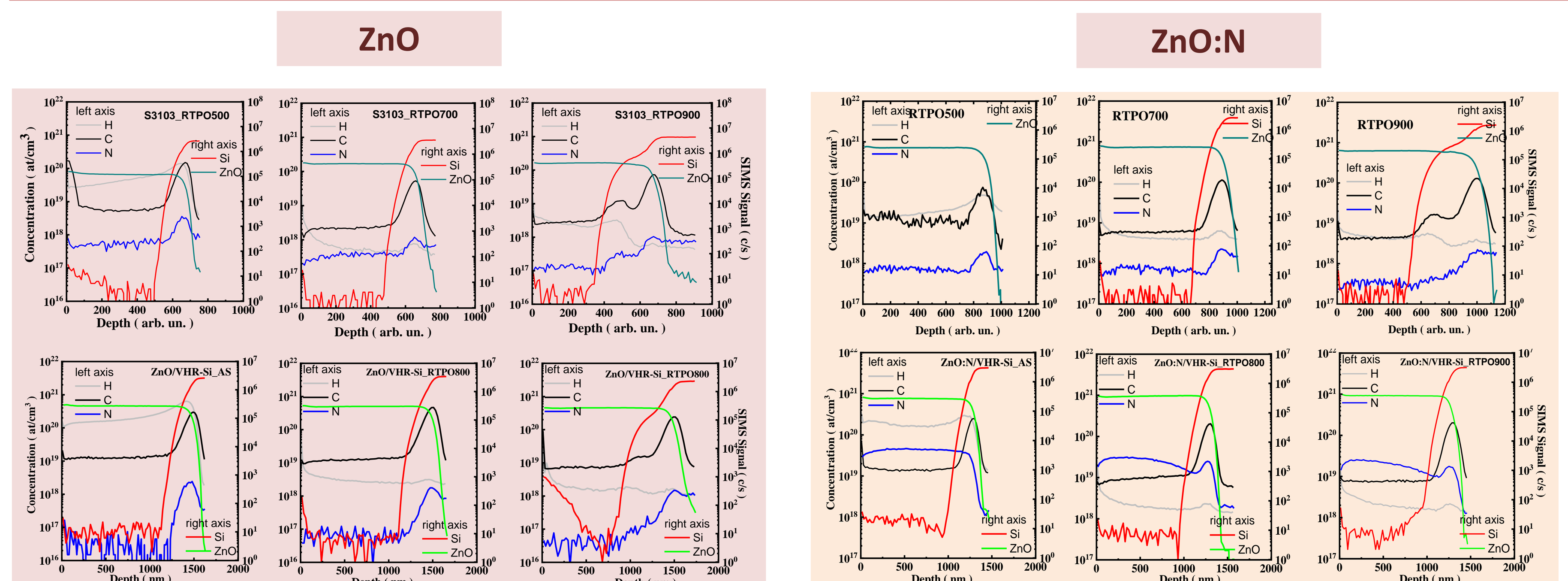
ZnO & ZnO:N on HR-Si(100)

1. Only two orientations, (110) and (100) observed in ZnO and ZnO:N
2. The (110) orientations is more pronounced probably due to lower strain experienced compare to the (100)

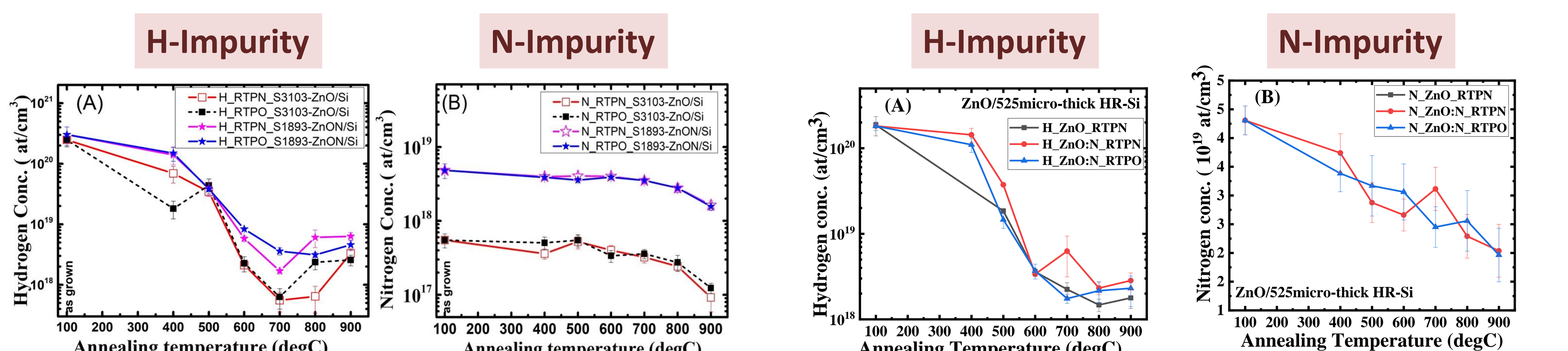
2. Crystallites size significantly enhanced after short 700RTP in both N2/O2 atmosphere.

3. Crystallinity highly improved after annealing at 900°C both ZnO and ZnO:N in both atmosphere.

Impurities in-corporation (SIMS)



1. Hydrogen impurities decreased up to two orders of magnitude after RTP>600°C temperature in both atmospheres
2. H-impurity is higher in case of ZnO:N annealed in N_2 atmosphere as compared to O_2 atmosphere
3. Nitrogen concentration in ZnO:N films does not depend on annealing atmosphere
4. Carbon concentration is at the level of 10^{20} at/cm^3 (lower in ZnO:N as compared to ZnO) and decreases to 10^{19} at/cm^3 after RTP>600°C in both atmospheres



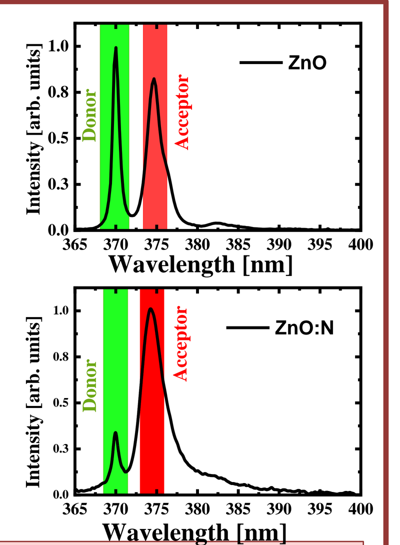
Low Temperature Cathodoluminescence with SEM Mapping

Excitation and recombination of electron-hole pairs drive CL emission in semiconductors. The CL maps can be used to detect radiative and non-radiative area of the film by scanning the incident beam across the sample.

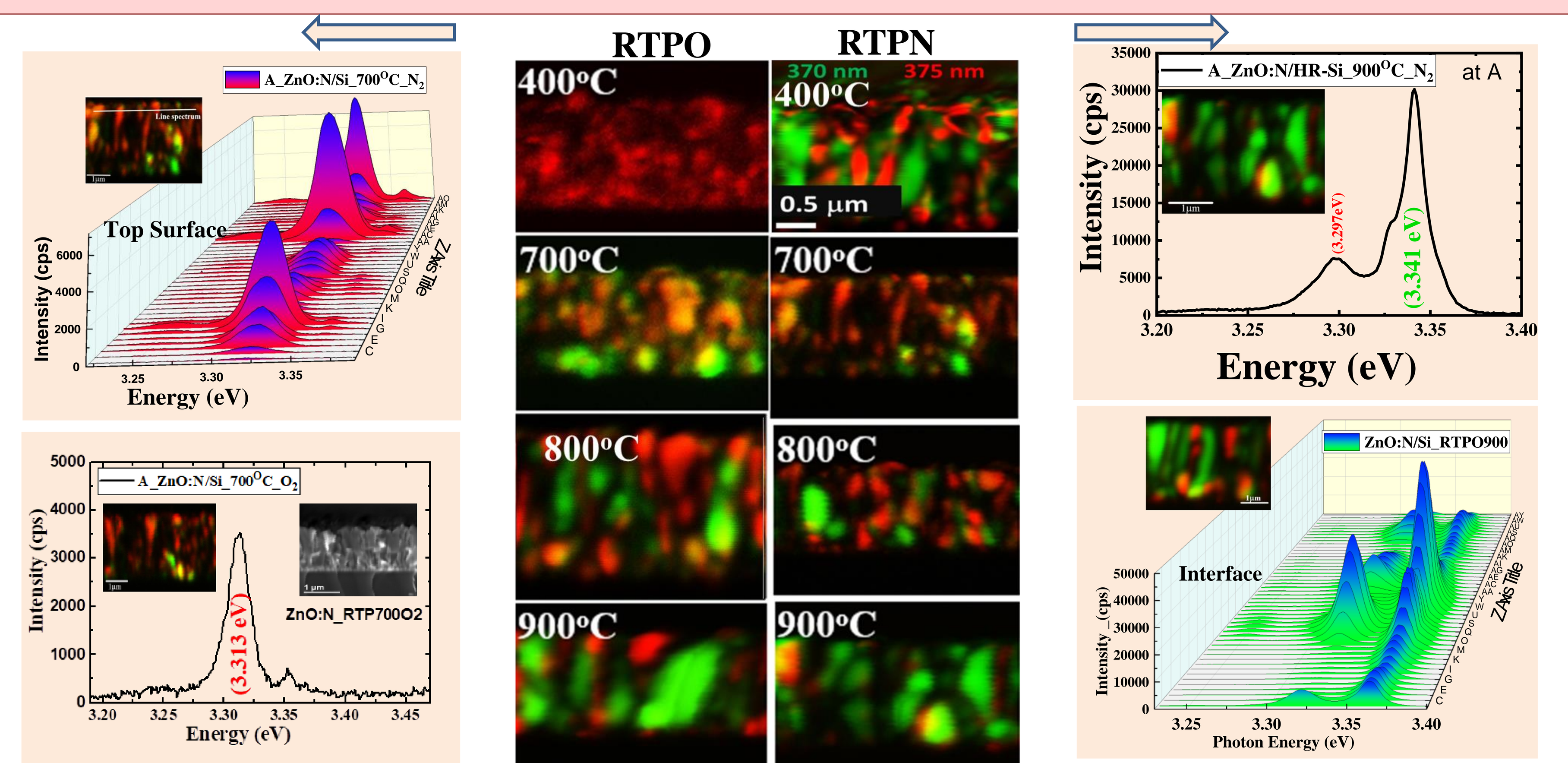
In the experiment, we recorded the CL maps from the ZnO and ZnO:N films cross-sections in order to investigate the spatial distribution of acceptor-related emission.

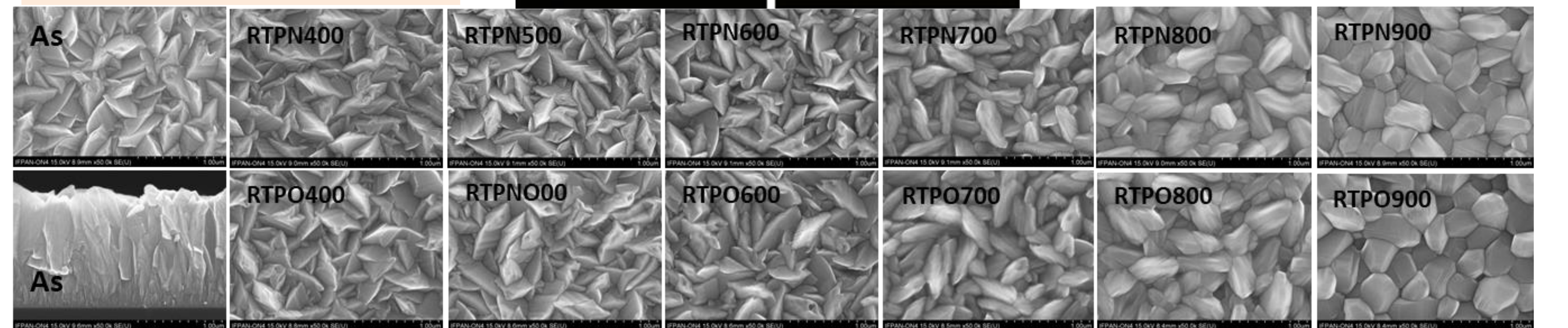
In case of ZnO and ZnO:N, the LT-CL spectroscopy can determine the status of acceptor or donor-related emission on given cross-section of SEM-image. To distinguish between optically active acceptor or donor-related lumenscence, LT-CL spectra were recorded at different cross-sections of ZnO and ZnO:N layers in the near band edge emission spectral region.

- LT-CL spectra and SEM images were recorded exactly at the same cross-section areas
- SEM and CL images were compared to relate the area of emission with the structure of the films.

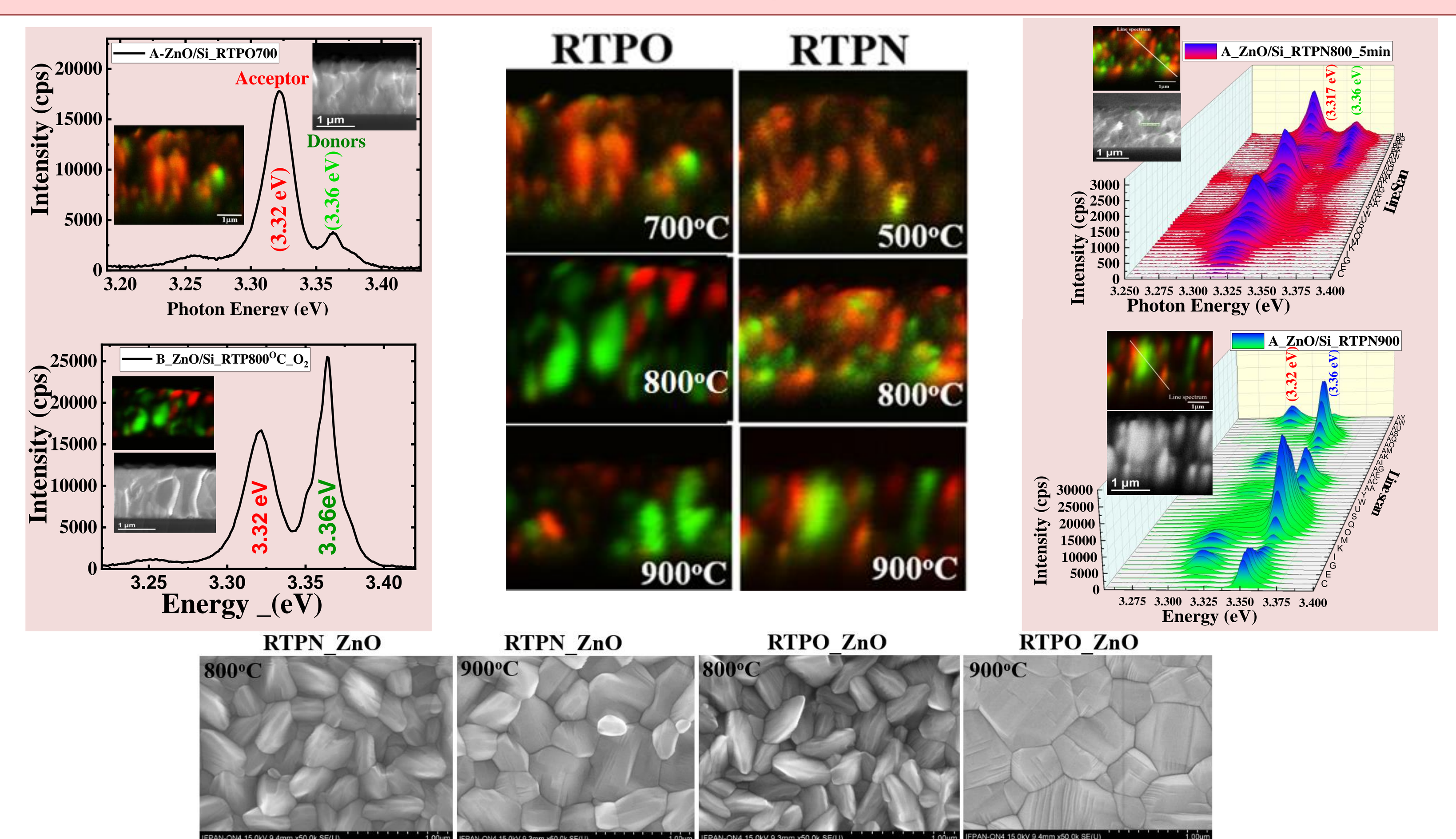


ZnO:N





ZnO



Conclusions

- LT-CL maps of ZnO and ZnO:N provide a complex picture in which acceptor- and donor-related CL separated and generally produced from distinct crystallites.
- Near band edge (NBE) CL is very weak in case of as grown films as well as films annealed at low temperature and also for higher N doping (> 10^{19}at/cm^3) and high H impurity concentration
- H concentration drops from 10^{20}at/cm^3 to 10^{18}at/cm^3 after RTP >600°C in both atmospheres; it was found to depend on resistivity as well as thickness of the silicon substrate (strain?)
- Both the annealing temperature and medium influenced the acceptor- and donor-related CL of ZnO and ZnO:N films, since they affect the concentration of N dopant, H and C- impurities as well as structural features of the films like strain and crystallite size
- Acceptor related CL emission is observed only for films annealed below 800°C; at 900°C annealing, more donors than acceptors get activated
- H impurity level is similar in as grown ZnO:N and ZnO, but it is 2-3 times higher for ZnO:N than ZnO after 700-900°C RTA which clearly indicates the presence of N-H bond and related complexes in ZnO:N films
- Scanning photoelectron microscopy study (SPEM) performed at Ellettra Syncrotrone Trieste with a *state of the art* resolution of 130 nm confirms the presence of *p*-type and *n*-type regions inside the ZnO and ZnO:N films (see Tuesday poster session TuPA27, *Electronic Structure of Acceptor Complexes in ZnO:N bulk and nanocrystals – DFT Calculations and Scanning Photoelectron Spectroscopy*)

References:

[1] Guziewicz et al., ACS Applied Materials & Interfaces 9 (31), 26143-26150, 2017.

[2] Mishra et al., "*Structural Properties of Thin ZnO Films Deposited by ALD under O-Rich and Zn-Rich Growth Conditions and Their Relationship with Electrical Parameters* " Materials 14.14 (2021): 4048.

[3] Guziewicz, Volnianska et al., *Valence Band Electronic Structure of ZnO and ZnO:N –Experimental and Theoretical Evidence of Defect Complexes,* Phys. Rev Applied (under revision)

Acknowledgement: The work is supported by research project No. 2018/31/B/ST3/03576 founded by the National Science Centre (Poland).