Low-temperature Cathodoluminescence of Nitrogen-doped ZnO Films Deposited at Low-temperature by Atomic Layer Deposition

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Motivation

In optoelectronics, the hurdle for wide application of ZnO is lack of stable p-type ZnO. Nitrogen is the most suitable acceptor among other dopants because it is closest to O in terms of atomic size and has been conclusively shown to act as a shallow acceptor in other II-VI semiconductors, namely, ZnSe, enabling LEDs [1]. Many research groups have reported p-type conductivity of ZnO by doping nitrogen as an acceptor but the results are not repeatable. According to recent reports, for the effective p-type doping with nitrogen, the ZnO oxygen-rich growth conditions play a vital role. Such conditions result in low formation energy of zinc vacancy defect [2], so the $V_{Zn}H$ and $V_{Zn}N_OH$ complexes, that provide shallow acceptor states, can be effectively created. According to our previous findings [3, 4], within the Atomic Layer Deposition (ALD) technique, acceptor conductivity of ZnO:N can be obtained at low growth temperature that ensures oxygen-rich conditions. Acceptor doping has to be activated by rapid thermal annealing at 800-900 °C which is confirmed by RT Hall measurement. RT conductivity has complex microscopic origin as shown by CL images in which donor and acceptor related emissions come from different regions.

In this research work, we are focused to analyze the ALD growth and post growth annealing conditions to achieve more intensive acceptor cathodoluminescence.

Experimental

Polycrystalline ZnO and ZnO:N of thickness 1.8 μm were deposited by ALD at 100°C on silicon substrates with 10000 ALD cycles.

DEZn and H_2O precursors were used as zinc and oxygen precursors followed by the reaction:

DEZn phase: ; surface - OH + C_2H_5- Zn - C_2H_5 → surface - O - Zn - C_2H_5 + C_2H_6

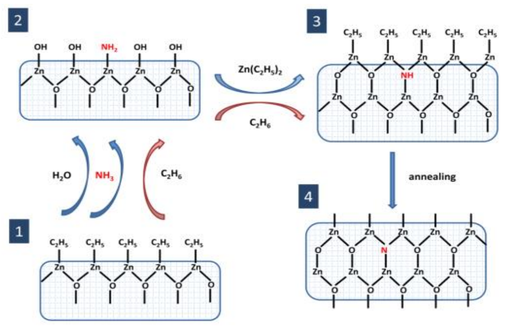
Water phase:; surface - O - Zn - C_2H_5 + H_2O → surface - O - Zn - OH + C_2H_6.

- Rapid thermal processing (RTP) at variable temperature (800 °C and 400 °C in O_2 and N_2, respectively)
- CL maps analyzed to find out the ALD growth and post growth annealing conditions to achieve more intensive acceptor luminescence
- XRD was done to analyze structural parameters of the films.

Ammonia water was used as a precursor for nitrogen doping (concentration of 10^{19} confirmed by SIMS) at every fourth ALD cycle according to the following incorporation of nitrogen.

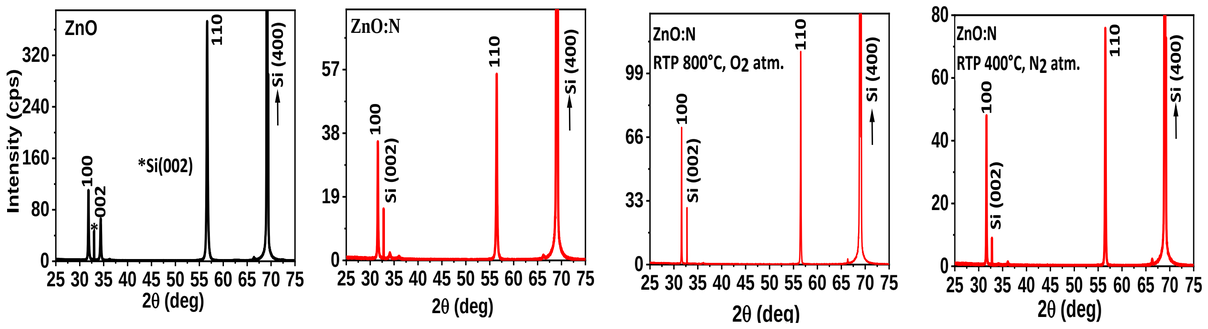
Ammonia water phase:; surface - Zn - C_2H_5 + NH_3 → surface - **NH_2** -Zn + C_2H_6

DEZn phase: surface - NH_2 . Zn - + C_2H_5- Zn - C_2H_5 → surface - **NH**- Zn - C_2H_5 + C_2H_6

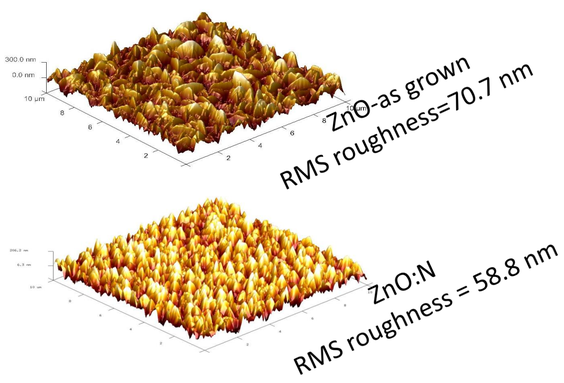


E. Guziewicz, et. al., *ACS Appl. Mater. Interfaces*, (2017)

Structural Morphology

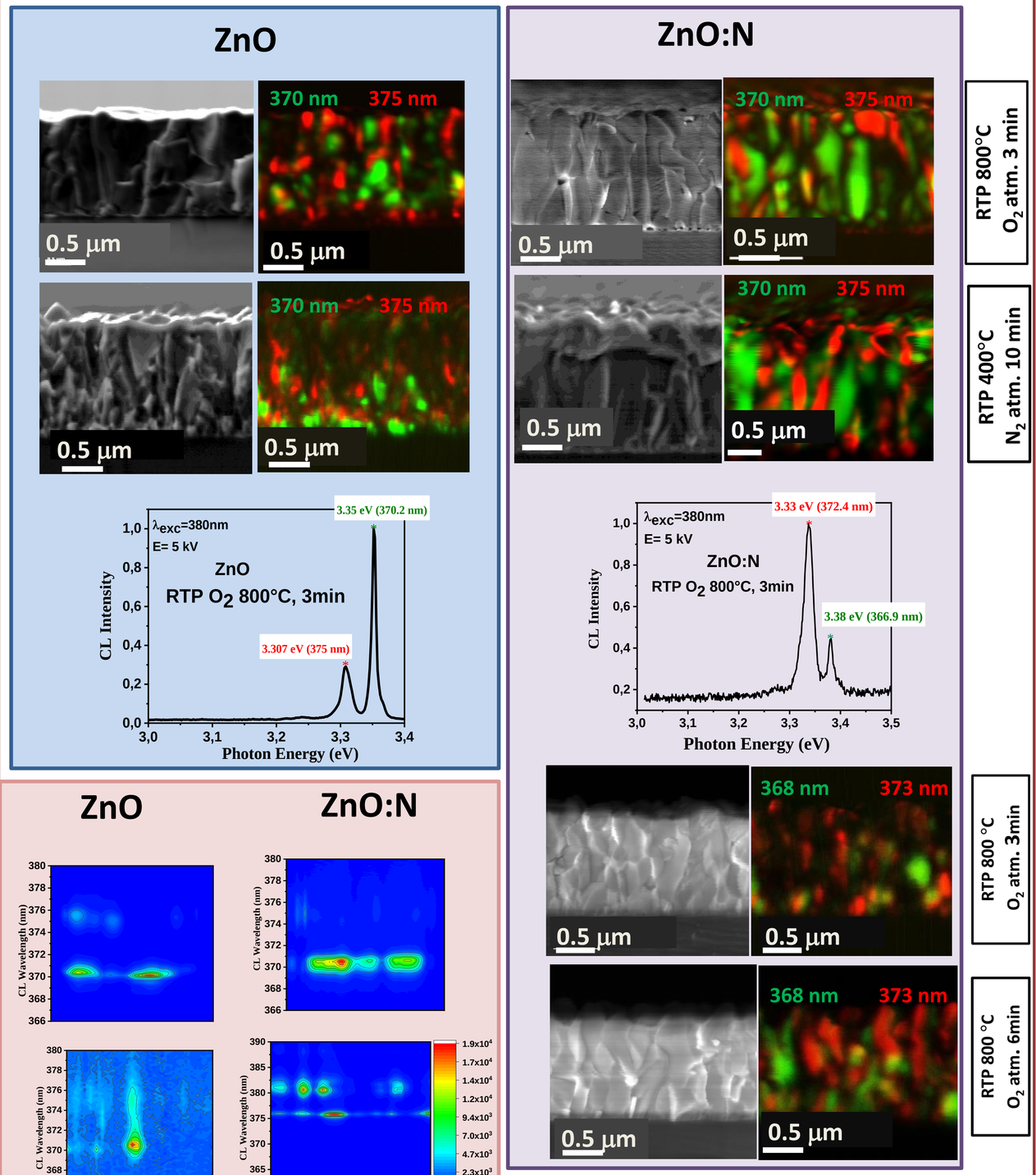


Sample	FWHM [°]			Crystallite size [nm]			Integral area percentage %			Dislocation density [Lines/cm^2] x 10^{10}			Average dislocation density [Lines/cm^2] x 10^8
	100	110	002	100	110	101	100	110	002	100	110	002	
ZnO	0.1592	0.2316	0.1915	51.880	38.949	43.418	13.645	75.983	10.371	3.715	6.591	5.304	14.218
ZnO:N-as grown	0.1228	0.1928		67.219	46.748		29.490	70.509		2.213	4.575		8.985
ZnO:N-RTP 800°C, O_2	0.1198	0.1198		68.896	75.259		28.204	71.795		2.106	1.765		4.005
ZnO:N-RTP 400°C, , N_2	0.181	0.1580		45.627	57.064		29.615	70.384		4.803	3.070		7.407

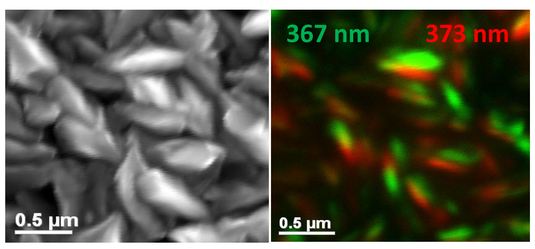


- **After nitrogen doping**
  crystallite size has increased and avg. dislocation density has decreased. **RMS roughness** of the films has decreased and morphology of the films has become more uniform. Peak 002 disappears in all the nitrogen doped samples.
- **Annealing of ZnO:N in oxygen atmosphere**
  crystallite size is increased and decrease in avg. dislocation density
- **Proportion of integral area (%)** of the peaks is similar after doping and annealing.

Cross sectional SEM image and CL map



Top view SEM image and CL map of ZnO:N-as grown



- Assignment of the donor- and acceptor-related peaks is based on temperature dependent photoluminescence studies of ZnO and ZnO:N films deposited by ALD with the same process parameters {*Przezdziecka et al. J. Appl. Phys., 2018 [4]*}
- Donor-related CL → ~3.35 eV (367-370 nm), donor-bound exciton recombination (D^oX) center
- Acceptor-related CL → ~3.31 eV (373-375 nm), free-to bound transition (FA) with acceptor binding energy of ~120 meV.

Conclusions

- Polycrystalline ZnO and ZnO:N films show 100 and 110 preferred orientations; the 002 orientation, which is present in ZnO, disappears in ZnO:N films.
- Nitrogen doping leads to the increase of the crystallite size; after 3 min. RTP in oxygen the grain size is further increased; longer annealing (6 min.) results in further increased crystalline size.
- Comparison of SEM and LT CL images of ZnO films reveal that acceptor and donor-related emissions derive from different micro-regions (crystallites) of the samples.
- In the ZnO films acceptor and donor-related regions are randomly distributed over cross-section of the film, but in ZnO:N the regions of acceptor emission are oriented along the columns of growth.
- Acceptor related emission is not originated from grain boundaries. It is also confirmed by XRD that after nitrogen doping, crystallite size increases so the surface area of grains decreases. It is evident that enhancement of acceptor-related emission is not related to grain boundaries.

References:
[1] Lyons et al., APL. **95**, (**2009**)
[2] A. Janotti & C.G. Van de Walle, *Rep. Prog. Phys*. 72, 126501 (**2009**)
[3] E. Guziewicz, E. Przezdziecka, D. Snigurenko, D. Jarosz, B. S. Witkowski, P. Dluzewski, and W. Paszkowicz, *ACS Appl. Mater. Interfaces*, (**2017**)
[4] E. Przezdziecka, E. Guziewicz, B. S. Witkowski, *J. Luminescence* (**2018**)

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