Study of point defects in ZnO thin films irradiated with alpha particles

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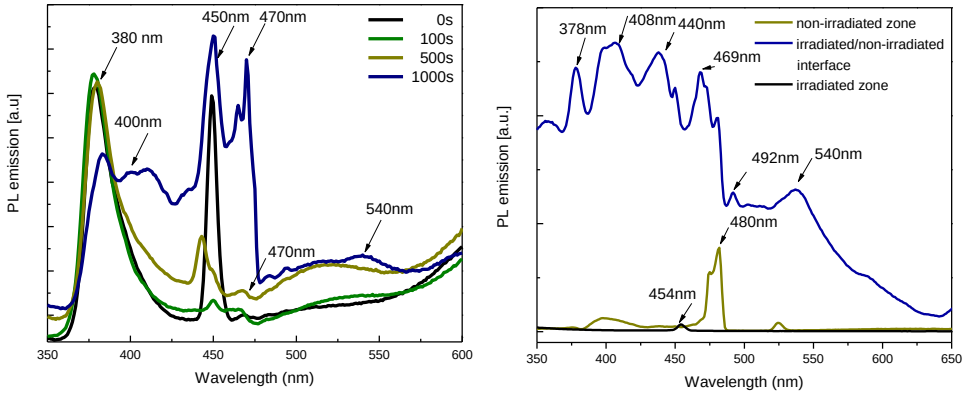
The effect of irradiation with alpha particles on the structure of ZnO thin films, and their optical and electrical properties has been investigated by scanning electron microscopy (SEM-EDS), atomic force microscopy (AFM), x-ray diffraction, optical transmission-absorbtion, photoluminescence and electrical measurements. Particularly, the photoluminescence (PL) of the films has been analyzed, aiming to evaluate the type and density of radiation-induced point defects as a function of the exposure time.

The films, prepared by sol-gel method, show the wurtzite-type structure, have thickness of about 100 nm, and average crystallite size of 21 nm. The optical transmission of the films in the visible region is 88% and the band gap energy, calculated from the absorbtion spectra is 3.24 eV. The PL emission spectra of the non-irradiated films exhibit emission peaks situated at 3.26 eV, 2.75 eV and a broad peak, with low intensity, in the region 2.60-2.25 eV. While the PL emission in the UV region is determined by free excitons band to band transitions, the emission peak in the green-orange region is related to radiative transitions involving native point defects in ZnO [1].

The films were irradiated with alpha particles at a doze of 5.3 kGy/h, the energy of 3 MeV, and the irradiation time was varied from 100 s to 500 s, to 1000 s and 8 h. The PL spectra of the irradiated films, presented in Fig.1(a), reveal the variation of the peaks intensity, as well as the presence of new emission bands, suggesting that radiative centers associated with point defects have been formed by irradiation. The PL emission in the region 3.10-2.30 eV exhibits an increased intensity with increasing the exposure time. New emission peaks appear at 3.10 eV, 2.64 eV and 2.30 eV in the PL spectrum of the films irradiated for 1000 s. Previously, the PL peaks at 3.15 eV and 2.90 eV were attributed to Zn interstitials (ZnI) and the PL peak at 2.40 eV was associated with the presence of oxygen vacancies (OVs) in ZnO [2, 3]. We suggest that the irradiation with alpha particles generates dispacement defects such as ZnI only for longer irradiation time (more than 1000 s), while the OVs are produced even after a short exposure time. The intensity of the PL peak corresponding to near band edge transitions decreases after a long exposure time, while the intensities of the emission peaks associated with point defects increase, suggesting that both ZnI and OVs act as efficient radiative centers.

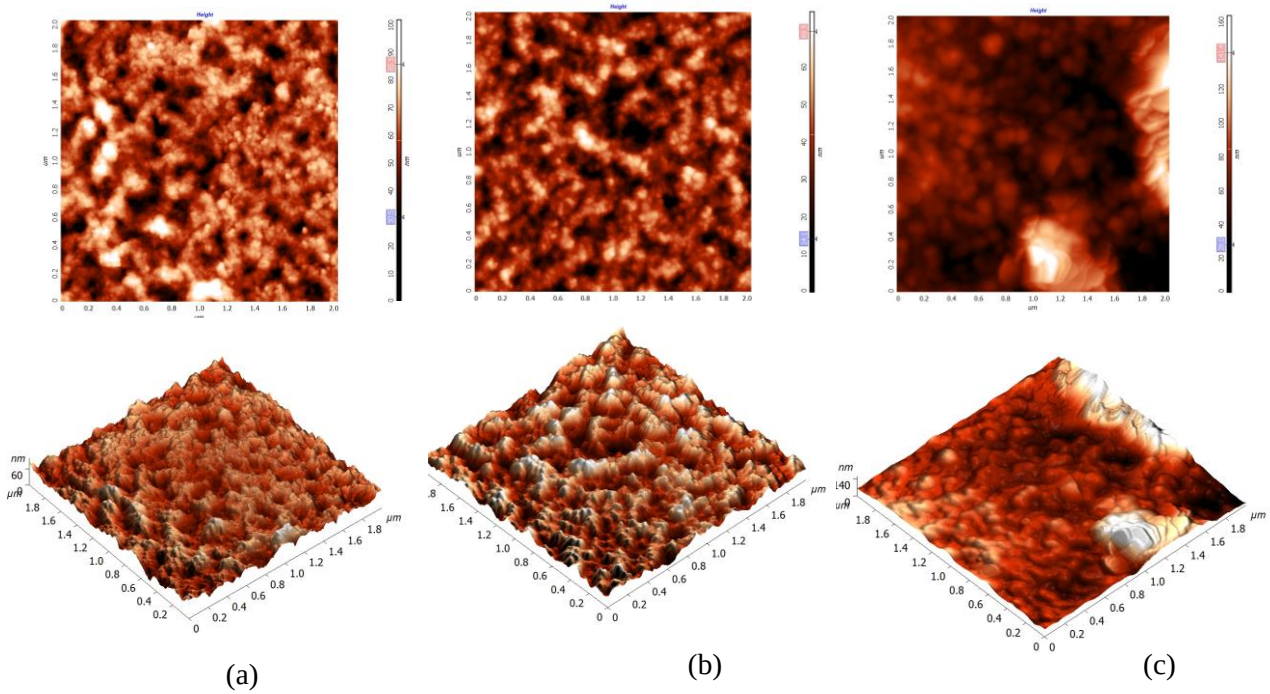
Fig. 1(b) displays the PL spectra of ZnO thin films after 8 h of exposure to alpha particles. The intensity of the PL emission appears strongly reduced, with a peak situated at 2.73 eV. The nearby region between the irradiated and non-irradiated zones yet demonstrates a series of well-resolved peaks located at 3.28-2.30 eV. The AFM 2D and their corresponding 3D images presented in Fig. 2(a)-(c) reveal that increasing the irradiation time determines the change of the surface morphology, with increased roughness and formation of clusters of grains particularly noticeable after 8 h of exposure to radiation. An increase in grain size and surface roughness after irradiation was previously reported in ZnO:B films irradiated with 80 MeV Br^{6+} ions and were related to the growth induced by energy loss [4]. The root mean

square roughness (R_{rms}) value of ZnO films surface resulted from AFM measurements on 2µm x 2 µm^2 area, decreases from 12 nm in unirradiated films to 11 nm in the films exposed to radiations for 500 s, Fig. 2 (a), and slightly increases up to 13 nm in the films exposed for 1000 s. The films irradiated for 8 h show a transition region at the interface between the irradiated and non-irradiated zone where the R_{rms} values are 11-15 nm, Fig. 2 (b). Inside the irradiated area presented in Fig. 2 (c), the R_{rms} in the localized zones containing clusters or large grains take values up to 23 nm, while in the somoother zones the value decreses to about 10 nm.



(a) (b)

Fig.1 Photoluminescence emission of irradiated ZnO thin films: 100-500 s (a) and 8h (b).



(a) (b) (c)

Fig. 2 Atomic force microscopy 2D and corresponding 3D images of ZnO thin films surface: (a) 500 s irradiated region, (b) 8 h irradiated/non-irradiated region, (c) 8 h irradiated region.

The x-ray diffraction patterns of the non-irradiated films and of the films exposed to alpha radiation for 8 h are presented in Fig.3. The peaks correspond to (100), (002), (101), (102), and (103) reflections of the hexagonal ZnO structure, with (002) texture. The (002) peak position shifted slightly from 34.45 to 34.37 and 34.43 in the nonirradiated, transition zone

and irradiated zone, respectively, as shown in the Table, suggesting the presence of in -plane residual stress. The intensity of the (002) peak decreses in the irradiated films, as well as the full-width at half-maximum (FWHM). The FWHM is influenced by grain size and stress distribution. The crystallites size increases from 22 nm in non-irradiated films to 23 nm in the irradiated ones, as presented in the Table, corresponding to the observed decrease of FWHM. The lattice constants remain unchanged, yet the residual stress is reduced both at the interface region as well as in the irradiated area of the films.

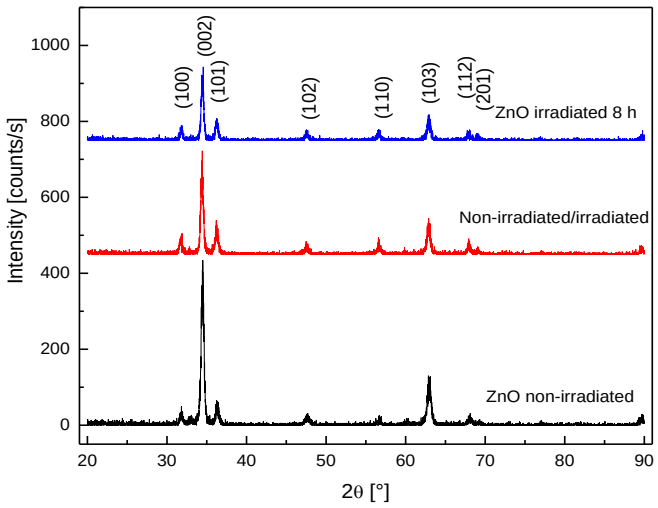


Fig. 3 X-ray diffraction patterns of the ZnO films.

Table. *The parameters of non-irradiated ZnO, non-irradiated/irradiated interface region and ZnO films irradiated for 8 h: 2θ, peaks height, FWHM, crystallite size, residual stress, σ.*

Films	Pos.[°2Th.]	Height [cps]	FWHM [°]	Crystallite size [nm]	σ (GPa)
Non-irradiated ZnO	(100) 31.78	289	0.41	21	0.19
	(002) 34.45	4992	0.40	22	
	(101) 36.21	582	0.44	20	
Non-irradiated/irradiated interface zone	(100) 31.64	441	0.38	23	0.08
	(002) 34.37	2888	0.38	23	
	(101) 36.23	772	0.47	19	
Irradiated ZnO	(100) 31.80	399	0.30	29	0.11
	(002) 34.43	2024	0.38	23	
	(101) 36.19	638	0.37	23	

The XRD data point out that the irradiation with 3 MeV alpha particles determines an increase in crystallite size in the film volume, besides the growth of the grains at the film surface and grains agglomeration, as observed in the AFM images. The growth of nanostructures on the ZnO thin films surface exposed to electrons or heavy ions has been attributed to a thermal annealing effect resulted by energy transfer from the incident particles, due to inelastic collisions. This effect could also account for the slight crystallite size growth and residual stress relaxation observed in the films volume in our study.

[1] A. Janotti and C.G. Van de Walle, Phys. Rev. B 76, 165202 (2007).
[2] H. Zang et al., Nucl. Instr. Meth. B 266, 2863–2867 (2008).
[3] E. Gűr et al., Nucl. Instr. Meth. B 266, 2021–2026 (2008).
[4] V. Kumar et al., J. Alloys Compd. 594, 32–38 (2014).