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Study of Microstructure and Elemental Micro-Composition of ZnO:Al Thin Films by Scanning and High Resolution Transmission Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

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Abstract. The microstructure and micro-composition of ZnO thin films doped with Al, deposited on Si/SiO_2 substrates by sol-gel method were investigated by scanning and high resolution transmission electron microscopy and related energy dispersive X-ray analyses (SEM-EDX, STEM-HRTEM/EDX). Thin films of ZnO were prepared by deposition of 1-10 successive layers with 0.5 at.% and 5 at.% Al concentrations. The evolution of the elemental composition, especially the Al concentration and distribution in the films with various number of layers were determined from energy dispersive X-ray spectra (EDS). The qualitative composition of the structures observed in the films have been evidenced in the elemental EDS maps.

Keywords: Al-doped ZnO films, sol-gel, nanostructures, SEM-EDX, HRTEM-EDX, STEM-EDX, elemental composition, elemental mapping.

1. Introduction

A wide range of applications, such as transparent conductors, electronic devices, UV detectors, solar cells, made that ZnO:Al doped thin films to be the subject of extensive studies in recent years [1–4]. A significant improvement of the films conductivity has been achieved by doping with group III elements: B, Al, Ga, In. Among them, Al has been proved as an excellent dopant, leading to a resistivity values of 1.2×10^{-4} Ω cm of sol-gel deposited films with 1.0 at.% dopant concentration [5]. It was reported that there is an optimum in the conductivity of ZnO thin films increasing by Al doping, explained by a limited incorporation of aluminium atoms into the ZnO lattice [6, 7]. Previous studies evidenced that structural characteristics and physical properties of sol–gel deposited ZnO:Al films are strongly affected by sols concentration with the dopant metal [8]. For instance, experimental results showed that aluminium concentration affect the crystallite size, determining the deterioration of the films crystallinity. The excessive dopant concentration did not enhanced carrier concentration, moreover it reduced the mobility, perhaps due to the higher probability of the impurity scattering [9]. Also, Al^{3+} dopants segregation into the grain boundary regions could be observed and found to determine the formation of an amorphous phase in polycrystalline Al doped ZnO thin film deposited on Si [10].

In this study we investigate the compositional homogeneity of ZnO:0.5% and 5% at. Al doped thin films deposited by sol-gel process on Si/SiO_2substrates. Energy dispersive X-ray analysis in the Scanning Electron Microscopy (SEM-EDX), Scanning and High Resolution Transmission Electron Microscopy (TEM-STEM-HRTEM/EDX) as well as Energy dispersive X-ray spectroscopy (EDS) mapping have been used to assess the nanoscale composition and local distribution of elements in the polycrystalline films.

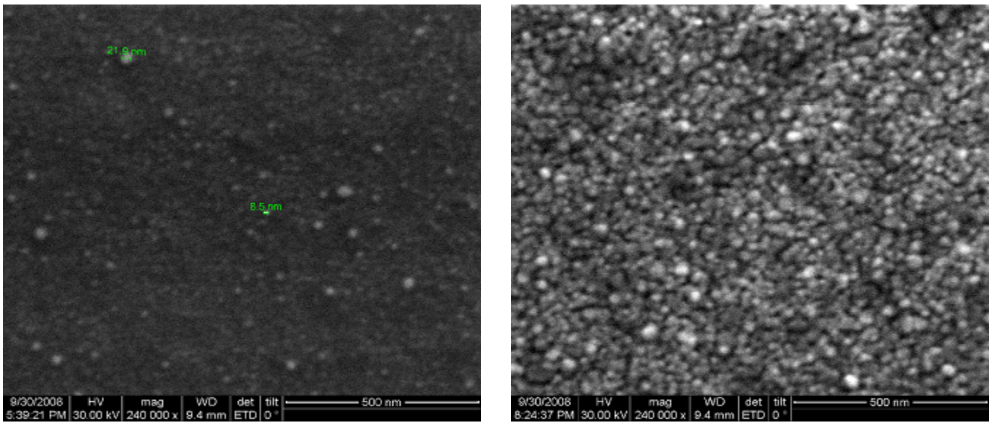
2. Experimental

ZnO thin films were deposited on Si/SiO_2 substrates by sol-gel method. The Al concentration was 0.5% at. and 5% at. The flowchart of the sol-gel deposition process was previously reported [11] and optical and electrical characteristics of the films with 1-10 layers were measured and reported [12]. The structural characteristics of the films were studied by X-ray diffraction (XRD) (Rigaku SmartLab with Cu K_α radiation) [12]. The microstructure and micro-composition of the films were investigated by scanning electron microscopy and energy dispersive X-ray (EDX) analysis using a SEM Quanta INSPECT F electron microscope, equipped with field emission gun – FEG with a resolution of 1.2 nm and a spectrometer for energy dispersive X-ray spectrometry (EDXS) with resolution of 133 eV to Mn K_α. The films structure and elemental composition analyses at nanoscale were performed using a high resolution transmission electron microscope TEM/STEM/HRTEM, TECNAI F30 with EDAX facility, operated at 300 kV.

3. Results and discussion

3.1. SEM–EDX and XRD analysis of the ZnO: 5% at. Al doped films

SEM images of ZnO: 5% at. Al doped films with 5 and 10 layers are shown in Figs. 1 (a) and (b). The films present nanograins with the size varying between 8.5–22 nm. We previously reported that the ZnO:Al doped films with wurtzite structure and preferential (002) orientation were obtained by sol-gel deposition on Si/SiO_2 substrates [11].



a) b)

Fig. 1. SEM images of the ZnO:5% at. Al doped films with 5 layers (a) and 10 layers (b).

XRD patterns of Al:ZnO films consisting of 5 and 10 layers deposited by dip-coating on the Si/SiO_2 substrates are presented in Fig. 2. The patterns were indexed according to the wurtzite structure (B4). The films are textured along the c-axis and perpendicular to the surface of the substrate, with the intensity of the (002) peak increasing with the number of deposited layers [12].

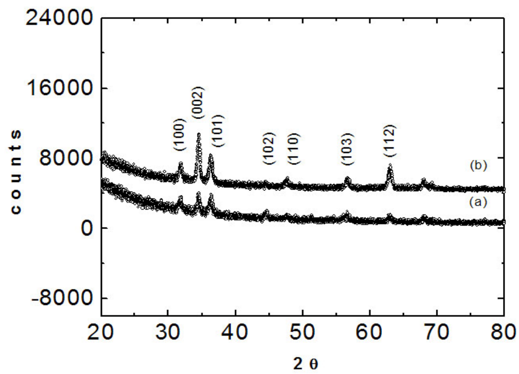
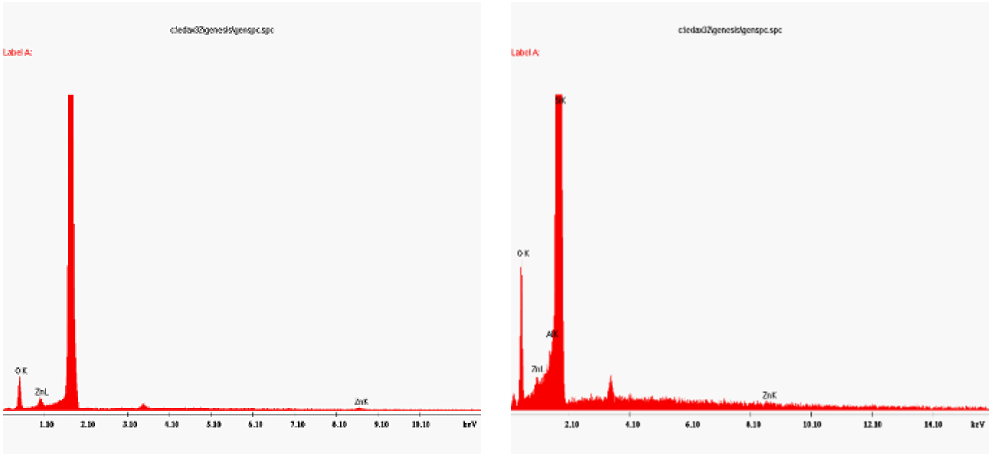


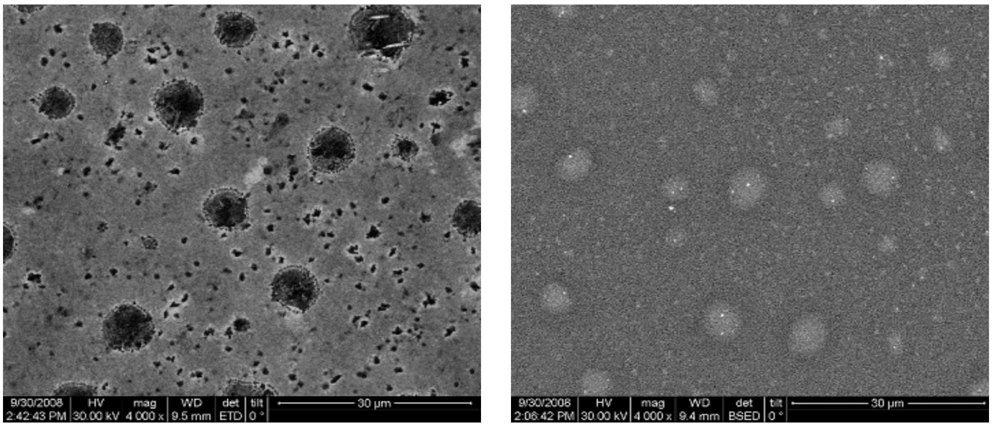
Fig. 2. XRD patterns of the ZnO:5% at. Al doped films with 5 layers (a) and 10 layers (b).

Figures 3 (a) and (b) show the EDX spectra of ZnO thin films presented in Fig. 1. The presence of the Zn L_α peak at about 1.010 keV, the Al K_α peak at 1.480 keV and the O K_α peak at 0.560 keV could be observed in the spectra. Previous studies showed that oxygen quantization through EDX is difficult to be achieved due to the O presence in the SiO_2 substrate [13].



a) b)

Fig. 3. Energy dispersive X-ray (EDX) spectra of ZnO: 5% at. Al doped films with 5 layers (a) and 10 layers (b).



a) b)

Fig. 4. SEM micrographs of the the ZnO: 5% at. Al doped film with 1 layer: backscattered electron image (a) and secondary electron image (b) show the microstructure of the first deposited layer. Regions with a higher Zn concentration appear as large rosettes in white colour (a) and black colour (b). The diameter of the rosette is about 10 μm.

In the doping process Al substitute Zn in the ZnO lattice, however, the distribution of the dopant ions in the films structure are still under investigation. Very recently, TEM investigation of ZnO: 2% at. Al doped polycrystalline films revealed a columnar structure of the grains and the presence of voids in the grain boundaries region. However, the Al, O, and Zn maps show a homogeneous elements distribution in the films [14].

In our study, the early stage of the films deposition was observed in the SEM images obtained using both BSED (Backscattered Electron Detector) and ETD (secondary electron detector) mode of SEM. The images are presented in Figs. 4 (a) and (b). Regions with a diameter of about 30 μm appear as white dots in BSED image from Fig. 4 (a) and with black contrast in the EDT image from Fig. 4 (b).

In order to correlate the microstructure and the distribution of O, Zn and Al, qualitative analyzes, *e.g.* elemental map and spectrum of the rosette region were recorded. The mapping images of O, Zn and Al elements are shown in Fig. 5 (a). The EDX spectrum from the same area is showed in Fig. 5 (b).

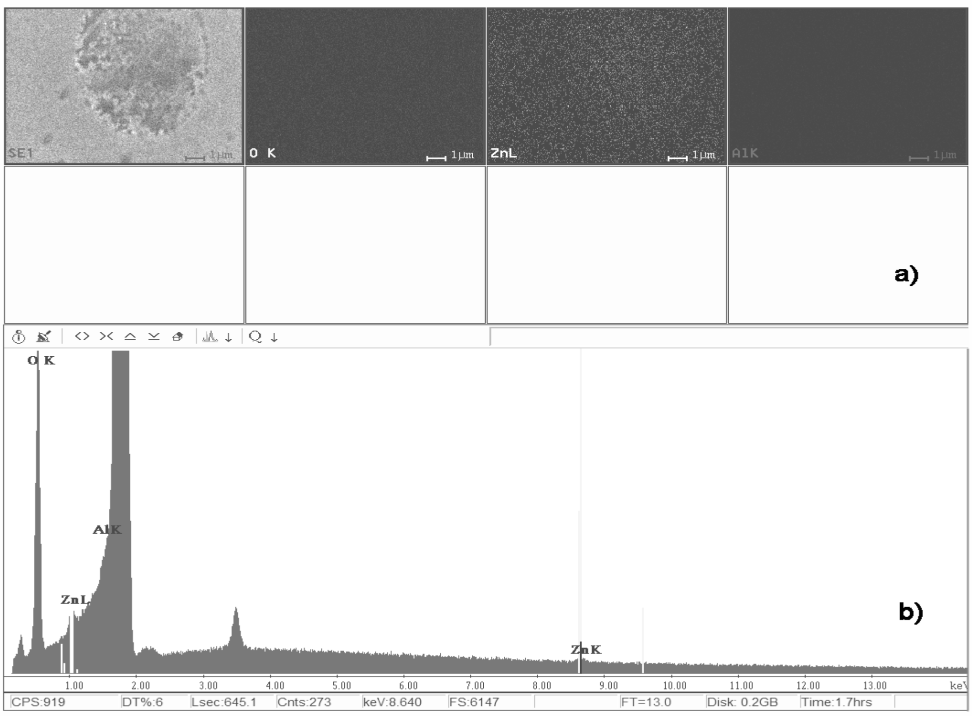


Fig. 5. Energy – dispersive X-ray spectroscopy mapping images of O, Zn and Al elements (a) and EDX spectrum (b) of the rosette area evidenced in Fig. 4.

The corresponding O and Al maps show a homogenous distribution of these elements. Contrary, the EDS mapping image of the Zn atoms evidenced bright spots equivalent to the rosette area and revealed an increased concentration of Zn atoms in these regions. We further investigated the films with an increased number of layers. We found the regions with Zn inhomogeneities in the films with up to 5 layers.

These regions diminished in the films with 6 to 10 layers, where Zn atoms concentration appears more uniform. SEM-EDX analyzes did not provided edifying results on the Al distribution due to the substrate influence against the films thickness in the characteristic X-rays generation.

3.2. STEM-EDX and HRTEM-EDX analysis of the ZnO:0.5% at. Al doped films

In order to investigate the nanostructure and the elemental distribution of the ZnO:0.5% at. Al doped films, STEM-EDX and HRTEM-EDX analyses of the films with 5 and 10 layers were performed on the plan view and cross section samples.

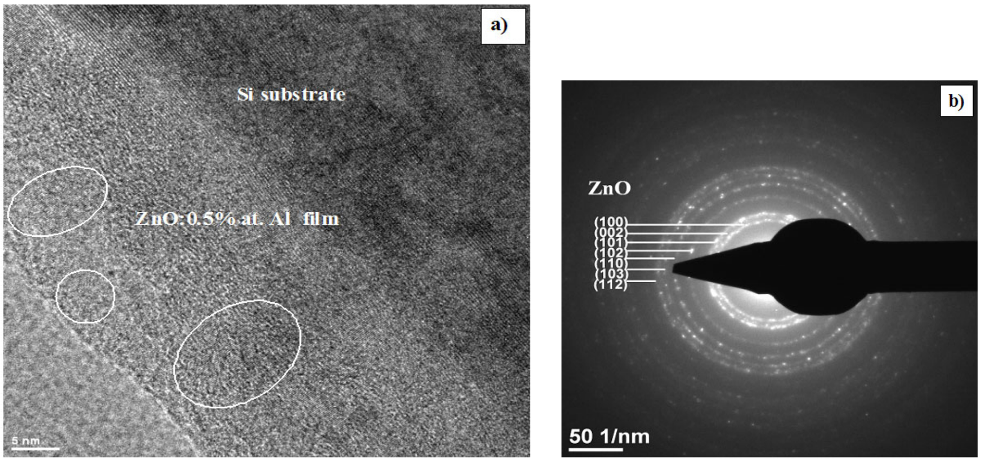


Fig. 6. Cross-section bright-field HRTEM images of ZnO:0.5% at. Al doped film with 10 layers deposited on Si/SiO_2 substrate (a) and selected area diffraction SAED (b).

Figure 6 shows a HRTEM cross section image of the ZnO:0.5% at. Al doped film (Fig. 6 (a)) and the selected aria electron diffraction image (SAED) (Fig. 6 (b)). The HRTEM image evidenced the presence of nanocrystallites randomly distributed in the ZnO film area Fig. 6 (a). The SAED image demonstrates the polycrystalline structure of the film with the indexed rings corresponding to wurtzite structure, according to previously results of XRD analyses (Fig. 2). The presence of large nanocrystalline grains, with the diameter of the film thickness, preferentially oriented on c-axis were observed in the HRTEM cross section images, Fig. 7.

The concentration of the Al ions in the films and their distribution was recorded both in the plan view and cross section of the films. Figure 8 (a), (b) presents a STEM image of the cross section from ZnO:0.5% at. Al film with 10 layers, (Fig. 8 (a)) and the EDX spectrum recorded in a point of a selected zone (Fig. 8 (b).

The entire marked area from the Fig. 8 (a) was divided into zones and an EDX spectrum was acquired in each zone. The qualitative and quantitative X-ray microanalyses and maps of the elements were obtained using the recorded EDX spectra.

The EDS maps of O, Zn, and Al shown in Fig. 9 evidenced a relative uniform distribution of the elements in the film area. The results of quantitative X-ray micro and nanoanalyses showed that Al concentration in the films with 5 layers was 0.35 ± 0.16 at.%. In the case of the film with 10 layers, Al concentration was 0.62 ± 0.08 at.%. The elemental composition of the films is presented in the Table 1 and Table 2.

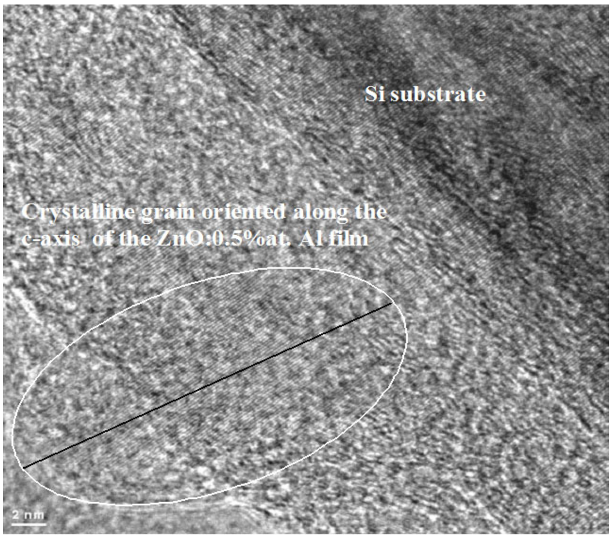


Fig. 7. Cross-section HRTEM image of ZnO:0.5% at. Al film with 10 layers deposited on the Si/SiO_2 substrate showing a nanocrystalline grain c-axis oriented.

Table 1. Elemental composition of the ZnO:0.5% at. Al film with 5 layers

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
O(K)	32.76	66.41	0.76	0.49	2.008
Al(K)	0.31	**0.37**	0.08	0.92	1.030
Zn(K)	66.92	33.20	0.92	0.99	1.68

Table 2. Elemental composition of the ZnO:0.5% at. Al film with 10 layers

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
O(K)	13.72	38.98	0.21	0.49	2.008
Al(K)	0.37	**0.62**	0.01	0.92	1.030
Zn(K)	75.51	52.48	0.38	0.99	1.686

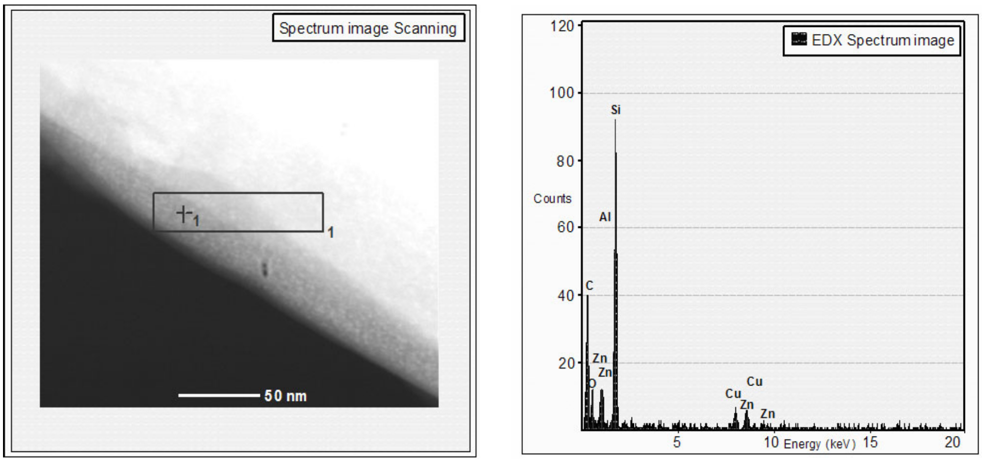


Fig. 8. (a) Scanning TEM (STEM) image of cross section sample from ZnO:0.5% at. Al doped film with 10 layers; (b) EDX spectrum recorded in the marked point from image (a).

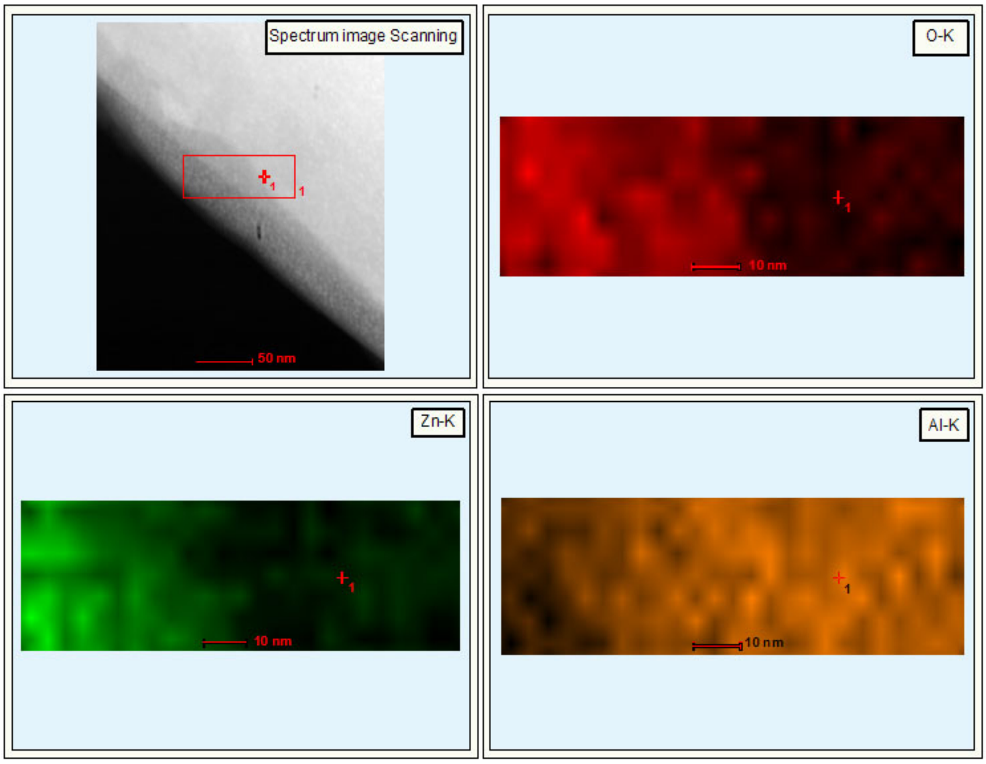


Fig. 9. Cross section STEM image of the ZnO:0.5%at. Al film with 10 layers on the Si/SiO_2 substrate and EDS mapping images of O, Zn, Al.

4. Conclusions

Micro-nanostructural and elements composition analyzes of ZnO:5% at. Al and ZnO:0.5% at. Al have been performed by SEM-EDX and HRTEM-EDX, STEM methods. The EDX spectra and elemental mapping evidenced that Zn distribution in the ZnO:5% at Al doped films is not uniform. An increased Al concentration in randomly distributed areas with about 10 μm diameter was observed in the films with up to 5 layers. A more uniform distribution of Zn was observed in the films with 5 to 10 layers. The concentration of Al in the films varied close to the doping values.

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