

PURE AND Lu(III)-DOPED  
NANOCRYSTALLINE ZnO FILMS BY CVD

Davide Barreca<sup>b</sup>, Giovanni A. Battiston<sup>a</sup>, Davide Berto<sup>a</sup>,  
Annalisa Convertino<sup>a</sup>, Alberto Gasparotto<sup>c</sup>,  
Rosalba Gerbasi<sup>a</sup>, Eugenio Tondello<sup>c</sup>, Sesto Viticoli<sup>d</sup>

<sup>a</sup> Istituto di Chimica Inorganica e delle Superfici del C.N.R., Corso Stati Uniti, 4 - 35127 Padova, Italy.

<sup>b</sup> Istituto di Scienze e Tecnologie Molecolari del C.N.R. and INSTM, Via Marzolo, 1 - 35131 Padova, Italy.

<sup>c</sup> Dipartimento di Chimica Inorganica, Metallorganica ed Analitica and INSTM - Università di Padova, Via Loredan, 4 - 35131 Padova, Italy.

<sup>d</sup> Istituto per lo Studio dei Materiali Nanostrutturati del C.N.R., Area della Ricerca di Roma, Via Salaria Km. 29.3, 00016 Monterotondo St. (Roma), Italy

Zinc oxide (ZnO) is a II-VI *n*-type semiconductor due to substoichiometries resulting from oxygen vacancies and interstitial zinc centres, that, in turn, give rise to shallow donor levels just below the conduction band edge (1). Because of their high conductivity and high transmittance in the visible region, ZnO-based thin films are widely used as transparent conducting oxides (TCOs) in optoelectronic devices such as solar cells, photodiodes, optical gas sensors and liquid crystal displays (2,3). In this context, rare earth (RE) ions incorporated in ZnO nanosystems are potentially very interesting as luminescent probes, due to their 4f intra-shell transitions, and can induce significant variations in the optical properties (4).

In this work we report preliminary studies on the synthesis of Lu(III)-doped ZnO thin films by the CVD technique. Lutetium has been chosen because the best results in doping ZnO with RE ions have been achieved by using elements with the lower atomic radius. To our knowledge, no previous reports on Lu(III)-doped ZnO thin films are available in current literature.

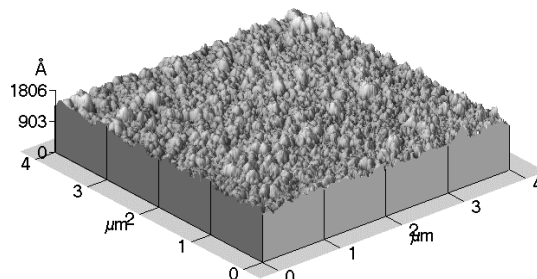
ZnO thin films were synthesised starting from  $Zn(C_5H_7O_2)_2 \cdot xH_2O$  (zinc(II) bis-(2,4 pentanedionate) hydrate) in  $O_2-N_2$  atmosphere in the temperature range 350–500°C. Lu(III)-doped ZnO thin films were deposited at 475°C using  $Lu(C_5H_7O_2)_3$  (lutetium(III) tris-(2,4 pentanedionate)) as lutetium precursor, starting from suitable  $Zn(C_5H_7O_2)_2 \cdot xH_2O$  and  $Lu(C_5H_7O_2)_3$  mixtures. The crystallinity and morphology of the films were analysed by X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Their chemical composition was investigated by X-ray Photoelectron and X-ray Excited Auger Electron Spectroscopy (XPS and XE-AES). Optical properties of the films were studied by UV-Vis spectroscopy.

XRD patterns indicated that ZnO films grew *c*-axis oriented up to 450°C and that an increase in deposition temperatures induced the formation of a non-oriented material. Such behaviour indicated a decrease of the texture with deposition temperature, which is due to a progressive loss of the *c*-axis orientation. The average crystallite dimensions calculated by the Scherrer formula were 30-40 nm. Concerning Lu(III)-doped ZnO films grown at 475°C, a shift in diffraction peaks towards lower  $2\theta$  values from the expected ZnO positions was observed and associated with the change in the lattice constants of zinc oxide nanoclusters. A possible explanation of this phenomenon might reside in the presence of oxygen vacancies, whose formation took place during film growth. In fact, thermal treatment in air at 500°C for 2 hours restored peak positions and, consequently, lattice constants to their bulk values, producing a concomitant increase in the crystallite dimensions. No reflections related to Lu oxides were ever detected.

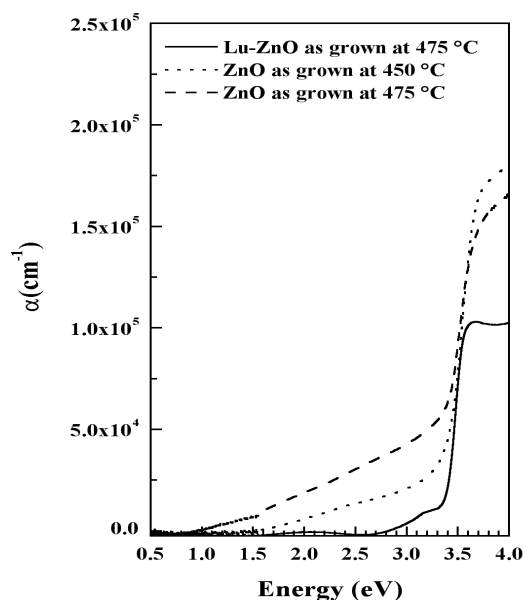
XPS and XE-AES investigations allowed us to ascertain film purity, a major concern for their optical and/or optoelectronic applications, and confirmed the formation of zinc (II) oxide irrespective of the synthesis

conditions. As regards Lu(III)-doped ZnO coatings, the  $Lu4d_{5/2}$  spin-orbit component was observed at a position of  $\approx 197.0$  eV, in substantial agreement with the value expected for  $Lu_2O_3$ . This observation does not contrast with the absence of  $Lu_2O_3$  XRD reflections, due to the relatively low average Lu content ( $\approx 4\%$ ).

Morphological AFM investigations (fig. 1) showed a granular-like surface texture, with average surface roughness ( $\approx 10$  nm) and grain dimensions ( $\approx 130$  nm) almost independent on Lu(III)-doping and processing conditions.



**Figure 1.** Representative AFM surface micrograph ( $4 \times 4 \mu m^2$ ) of an *as-prepared* Lu(III)-doped ZnO film deposited on a glass substrate at 475°C.



**Figure 2.** Energy dispersion of the absorption coefficient  $\alpha$  for pure ZnO films grown at 450°C and 475°C, and for Lu(III)-doped ZnO film grown at 475°C.

Concerning undoped ZnO films, variations of the growth temperature between 450°C to 475°C produced an increase of the Urbach tails observed below 3 eV in fig. 2. These results can be ascribed to a higher structural order at lower deposition temperatures, as observed from XRD analyses. Lu(III) doping improved the transparency of the pure ZnO films (fig. 2); in fact, the Urbach tails were almost negligible for the doped film. This phenomenon might suggest a contribution of lutetium oxide in the Lu(III)-doped film, in agreement with XPS results.

1. H.L. Hartnagel, A.L. Dawar, A.K. Jain, and C. Jagadish, in *Semiconducting Transparent Thin Films*, Institute of Physics Publishing, London, UK (1995).
2. S. Major and K.L. Chopra, *Solar Energy Mater.*, **17**, 319 (1988).
3. K. Belghit, M.A. Subhan, U. Rulhe, S. Duchemin and J. Bougnot, in *10<sup>th</sup> European Photovoltaic Solar Energy Conference*, p. 613, Lisbon, Portugal (1991).
4. M Liu, F-Q. Liu, H-Q. Guo, Z-H. Zhang and Z-G. Wang, *Phys. Lett. A*, **271**, 128 (2000).