

# Strain effect on the green and red emissions of ZnO:Zr thin films deposited by spray pyrolysis

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**Abstract**—The structural, morphological and cathodoluminescent properties of zirconium doped zinc oxide thin films deposited by reactive chemical pulverization spray pyrolysis technique on heated glass substrates at 450 °C are being reported. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and cathodoluminescent (CL) spectroscopy. CL spectra have revealed three CL peaks: a near-band edge emission (NBE) with peak positioned at 382 nm, a green emission at 520 nm, and a red emission around 672 nm and 755 nm. The origin of the observed emission bands is discussed.

**Index terms** - ZnO, Zr, Spray Pyrolysis, Strain, Thin films.

## I. INTRODUCTION

ZnO is a II-VI group wide band-gap compound semiconductor. At room temperature, it has a wide band gap of 3.37 eV and a large exciton binding energie of 60 meV. Many experimental results show that ZnO has an excellent excitonic emission performance, so it is an ideal material for the fabrication of short-wavelength optoelectronic devices, especially for the fabrication of ultraviolet light-emitting devices such as ultraviolet light-emitting diodes, ultraviolet lasers, etc. ZnO materials usually show two luminescent regions: a narrow ultraviolet peak and a visible luminescence. For the ultraviolet emission, it is generally attributed to transition of electrons between valence band and conduction band or/and recombination of free excitons [1,2] therefore, the ultraviolet emission is closely connected with the density of free exciton in ZnO thin films. The existence of this band indicates on the crystalline quality of the films in fact that the density of free exciton is directly associated with this later. However, for the visible part of the luminescence spectrum, although lots of searches, visible emission mechanism is controversial as yet. The visible luminescence is mainly due to the structural defects in ZnO which are related to deep level emission, such as oxygen vacancy, zinc vacancy, interstitial zinc and interstitial oxygen [3,4].

According to Kang et al [5] and Shan et al [6], they attribute the green emission to oxygen vacancies in ZnO thin films. But the researches of Liu et al [7] ascribe it to oxygen interstitials. The results of theoretical calculations on the energy levels of intrinsic point defects in ZnO have indicated that ionized oxygen vacancies  $Vo^+$  produce a deep donor level 2,4 eV at the bottom of CB [8] this value is more close to 520 nm found in our experiment. Lima et al [9] have suggested that green emission should be attributed to the lowest lattice micro-strain.

For the emissions in the wavelength range of 672–755 nm may originate from oxygen defects.

Some research results show that surface states of the films play an important role in the luminescence [10] and still others think that the red emission correspond to the structural defects .

In our previous work [11,12], we have reported the preparation of ZnO:Zr thin films using spray pyrolysis method on glass substrate and analysed the properties variation of zirconium with the deposition temperature and surface roughness, in this paper we have prepared the ZnO:Zr thin films and mainly investigated their Cathodoluminescent properties.

## II. EXPERIMENT DETAILS

ZnO and ZnO:Zr thin films were deposited by spray pyrolysis. The spraying solution was 0.05 M zinc chloride. Zirconium doping was achieved by adding  $ZrCl_4$  in a concentration of 3, 5, 7, and 10 at.%. The solution flow rate is set to 5 ml/min onto the clean glass substrates heated at 450 °C using compressed air as carrier gas. The deposited time was 6 min. the nozzle was fixed and its diameter was 500  $\mu$ m. The nozzle to substrate distance was about 40 cm. The structural characterizations are performed using X-ray diffraction (XRD) with Cu  $K\alpha$  radiation ( $\lambda=1054$  Å). The surface morphology was examined by scanning electron microscopy (SEM). The composition was studied by X-ray photoelectron spectroscopy

(XPS). XPS measurements were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA, during measurements the pressure was 10<sup>-6</sup> Pa. The excitation source window was aluminium. The energy calibration of the spectrometer was done using gold and copper plates fixed on the sample holder. The cathodoluminescence set used was a homemade system developed to perform near-field cathodoluminescence (CL) microscopy [13]. This one is based on the combination of scanning force microscope (SFM) and field emission scanning electron microscope (FESEM GEMINI 982 from LEO); its mechanical details are reported by Troyon et al [13]. The CL spectra were from well-defined spots of the sample with a fixed electron beam at low accelerating voltage (5 keV). The photons were collected with a multimode optical fibre (NA = 0.48) placed close to the sample surface (~50 µm) and analyzed with a spectrometer that has had a spectral resolution of 0.5 nm and was equipped with an N<sub>2</sub>-cooled CCD detector. All spectra were acquired at room temperature.

### III. EXPERIMENTAL RESULTS

The structural properties of the undoped and zirconium doped ZnO grown at 450 °C with an atomic concentration of 3, 5, 7 and 10 at.% are analyzed by XRD patterns in figure 1. It can be found that all the films are polycrystalline with the hexagonal Wurtzite structure and have a preferred orientation with the c axis perpendicular to the substrates. The crystallinity is improved by 5 at.% zirconium indicated by the high (002) peak intensity (FWHM = 0.2°). Any additional peak has been observed. It reveals that presence of Zr in ZnO keeps the preferred textural growth orientation (002). It is in good agreement with the earlier work for films prepared by radio frequency magnetron sputtering technique [14]. The mean crystallite size D was calculated from the (002) diffraction peak using Scherrer's formula [15]. Values of D are 32.8; 36.9; 39.6; 35.3 and 31.9 nm respectively for undoped, 3, 5, 7 and 10 at.% of Zr. We conclude that the films, which present a higher XRD intensity, have a strong grain size therefore a good crystallinity.

Scanning electron microscopy (SEM) images (see Fig. 2) have revealed that undoped ZnO thin films present compact surfaces covered with mainly hexagonal grains. It can be seen that the insertion of zirconium changes the crystallites shape. When dopants are introduced during the forming process of nanostructures, they affect the conditions of ZnO crystal growth. We can notice that the doped films are characterised by porous and rough surfaces excepted 5 at.% Zr doped ZnO thin films which show a well separated and oriented crystallite with a little less empty.

The XPS spectra of Zn 2p and Zr 3d for the 5 at.% Zr film are shown in Fig. 3. The binding energy of Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> are located at about 1023.16 eV and 1046 eV respectively (fig. 3a) which indicate that most Zn atoms exist as Zn<sup>2+</sup> in the ZnO structure [16]. In Fig. 3b two predominant

peaks are observed at binding energies of about 183 eV and 185.6 eV assigned to Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> respectively, implying that Zr is in the state of Zr<sup>4+</sup> [17].

The calculation of the films strain is based on the biaxial strain model [18]. The strain along the c axis, i.e. perpendicular to the substrate surface, was measured by the relationship below. The c axis lattice parameters can be calculated from the XRD patterns.

$$\varepsilon_{zz}(\%) = \frac{C_{film} - C_{bulk}}{C_{bulk}} * 100$$

Fig. 4. displayed the strain of the films as function of the zirconium concentration. We can see that the strain  $\varepsilon_{zz}$  in the films decreases first suggesting that Zr<sup>4+</sup> ions substitute Zn<sup>2+</sup> ions due to their small ionic radius (0.72 Å) compared with that of Zn<sup>2+</sup> (0.74 Å), to reach a minimum for samples doped 5 at.% of Zr indicating the existence of relaxed films. This means that the texture of the layers becomes better which is in agreement with the morphology and the XRD diffraction of the films as shown in Fig. 4. When the Zr content exceeds 5 at.%, the strain of the films increases indicating that Zr atoms occupied the interstitial positions. It appears from this study that the crystallinity and the surface of thin films depends on the doping concentration. This parameter affects the stresses introduced during growth. In conclusion, growth layers with low stress leads to well-crystallized thin film with smooth surfaces.

Fig. 5 shows emission spectra of Zr doped ZnO thin films, the emission spectrum consists of UV peak for all samples. This luminescent band reaches the maximum intensity for 5 at.% Zr doped sample. This enhancement of the UV band is intimately connected to the crystalline quality of the layers in concordance with X-ray results which show that the 5% Zr doped sample present the best crystallinity. This behaviour could be due as well to an increased rate of donor bound excitonic recombination, along with increase of electronic population in conduction band brought by formation of shallow donor level. As the donor bound excitonic recombination prevails, it seems that charge transfer rate to the recombination sites for visible light emission diminishes. In fact we can notice that a decrease of the UV emission is accompanied by a sharp increase of the red band. The existence of the centre responsible for this band results in the quenching the UV luminescence [19].

Therefore, the origin of the red should be discussed taking account of the structural defects caused by the incorporation of Zr into the ZnO lattice, in fact that our layers have a varying rate of crystallinity. For films doped 5 at.% of zirconium which have a less defects than the other films, it seems that the emission in the red range diminishes and a green emission is slightly more important in this case, we think that this later mainly resulting from the lowest strain of films according to results of Fig. 4.

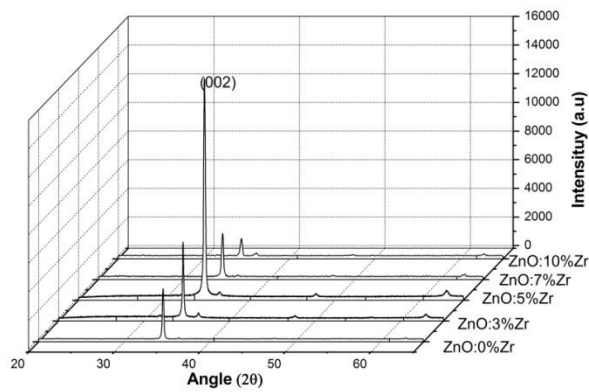


Figure 1. X-ray diffraction spectra of undoped and Zr doped ZnO thin films.

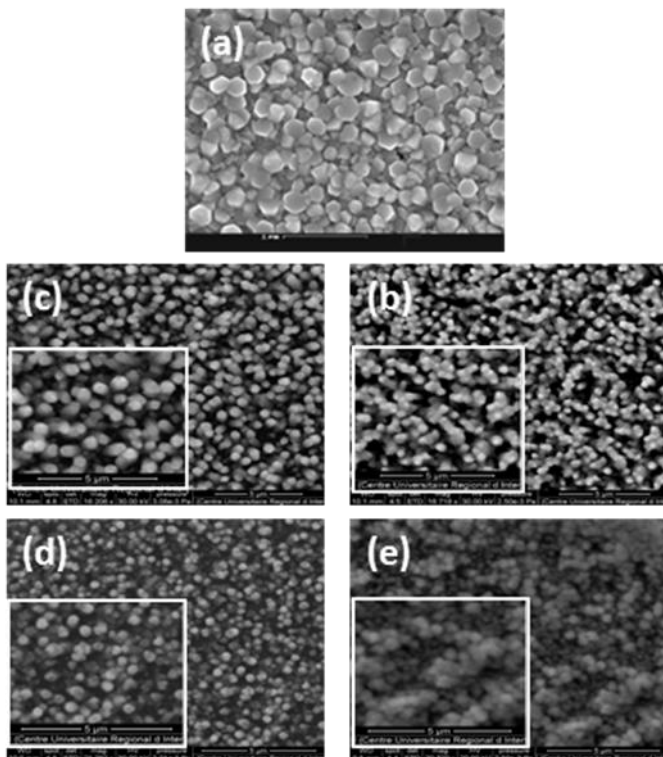


Fig. 2. SEM micrographs of: (a) undoped (b) 3 at.% (c) 5 at.% (d) 7 at.% and (e) 10 at.% Zr doped ZnO thin films.

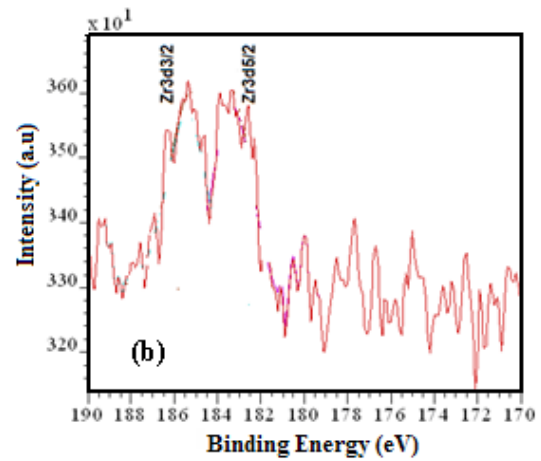
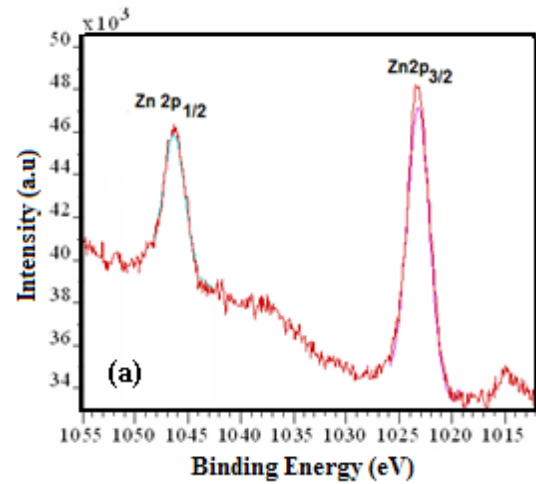


Fig. 3. XPS spectrum of (a) Zn 2p and (b) Zr 3d for ZnO:Zr 5 at.% thin films deposited at 450 °C

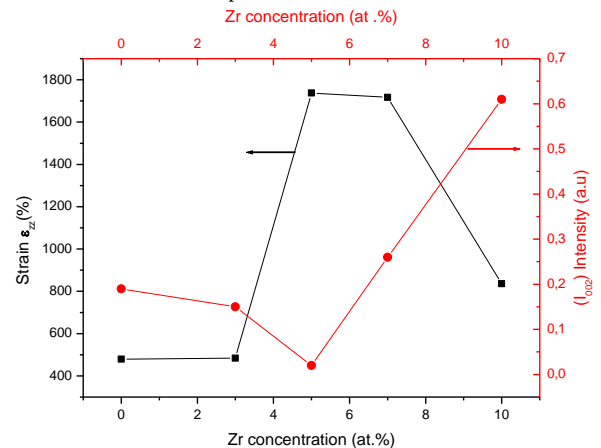


Fig. 4. Strain and the (002) intensity ( $I_{002}$ ) of films as a function of Zr concentration.

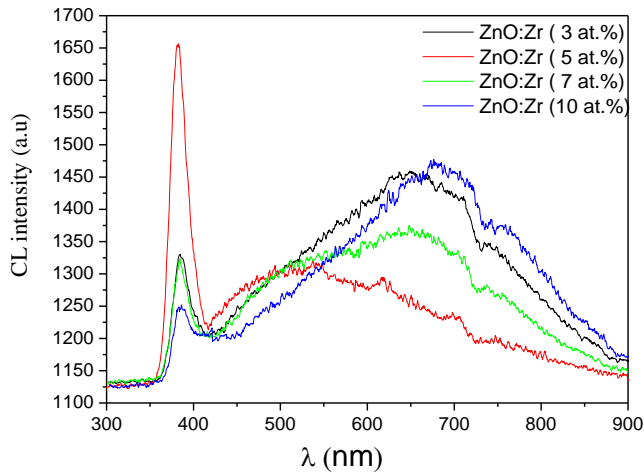


Fig. 5. Cathodoluminescence emission of Zr doped ZnO films at different level doping.

#### IV. CONCLUSION

Thin films of Zr-doped ZnO oxide have been deposited onto glass by spray pyrolysis. The results of cathodoluminescence measurements show that ZnO:Zr nanostructures exhibit a three peaks: a near UV at  $\lambda = 382$  nm, a green emission at  $\lambda = 520$  nm and a weak red range at  $\lambda = 672$ -745 nm. The above experiments reveal that ZnO films with different structures or defects will show different cathodoluminescence properties. The 5 at.% Zr doped ZnO spectra shows a strong UV emission, and a weak green emission with no red emission. The effective enhancement of the film's UV emission can be achieved by the improvement of the film crystalline quality. However, the existence of green emission may result in the lowest strain of nanostructure films. The presence of an intensive red light typical of the structural defects of the material.

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