Surfaces and Interfaces 8 (2017) 176–181

Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.elsevier.com/locate/surfin

# Fluorine dopant concentration effect on the structural and optical properties of spray deposited nanocrystalline ZnO thin films

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ARTICLE INFO

*Keywords:*
Spray pyrolysis deposition
ZnO and ZnO:F thin films
Structure properties
Optical band gap
B.M effect

ABSTRACT

Pure and fluorine highly doped Zinc oxide with different concentrations (0.1,0.2,0.3 mol/ℓ) thin films were deposited on glass substrates heated up to 450 °C by chemical spray pyrolysis (CSP) technique. They were characterized using various techniques. X-ray diffraction pattern showed that all films had a polycrystalline structure Hexagonal wurtize phase; the doping processes did not show an obvious effect on the films structure. Structural parameters such as inter-planer distance, lattice constants, average grain size, dislocation density, the number of crystallites per unit surface area and strain could be determined as a function of Fluorine dopant concentration. The prepared films Grain size was found to be ranged from 39 to 52 nm, which indicates that all films have nanocrystalline structure. SEM images demonstrated a homogeneous and smooth uniform surface, and EDXS spectra confirm the stoichiometry of the deposited films. Optical properties data of the prepared films showed high transmittance values in the visible region (i.e. 40–99%), and this was increased after the doping process therefore the ZnO:F film was very suitable for solar cells applications . The energy gap ($E_g$) of direct electronic transitions was found equal to (3.082 eV) for pure ZnO and it increased to (3.163, 3.256, 3.271 eV) for ZnO:F, this behavior could be attributed to the Burstein–Moss effect.

## Introduction

Zinc oxide (ZnO) is belonging to the II–VI group compound semiconductors. ZnO thin films are very promising materials and attracting considerable attention due to its suitable optical and electrical properties [1,2]. It can be considered as an alternative for transparent conductive films if it doped with suitable impurities due to the fact that a high transmittance and low resistivity can be obtained simultaneously [3]. Transparent conducting oxide (TCO) films have an extensive applications in optoelectronic devices [4], TCO have a high electric conductivity and a high visible transmittance together with a wide direct optical band gap. Zinc oxide is practically useful as a transparent conducting oxide due to its large band gap (3.37 eV) [5,6], high conductivity, easily doped and thermally stable [7]. Additionally Zinc oxide thin films have widely been investigated due to their important applications namely, as transparent electrode, antireflection coating and windows in solar cell, gas sensors and in optoelectronic and piezoelectric devices [3–7]. The effective way to enhance the optical and the electrical properties of ZnO is by doping it with Aluminum, fluorine etc. [3,8,9].

ZnO and ZnO:F can be prepared adopting many techniques including metal-organic chemical vapor deposition (MOCVD) [10], nonreactive radio frequency (RF) magnetron sputtering [4], DC magnetron sputtering [5],sol-gel spin coating [11], pulsed laser deposition (PLD) [12] and spray pyrolysis [13,14], electron beam deposition [15]. In this study pure and Fluorine highly doped ZnO thin films were deposited by low coast spray pyrolysis technique at 450 °C substrate temperature; it is the most convenient method because of its simple,low cost, ease to add doping materials and the possibility of enhanced the film properties by the composition variation of starting solution.

## Experimental work

Zinc chloride ($ZnCl_2$) and Ammonium Fluoride ($NH_4F$) were used to prepare the precursor solutions of pure and Fluorine doped ZnO and thin film. 3.407 g of $ZnCl_2$ was dissolved in 250 ml of distilled water by heating to 90 °C for 15 min to obtain 0.1 Molarity concentration of $ZnCl_2$ solution. To getting Fluorine doping . Three $NH_4F$ solutions with different molarity concentrations (0.1, 0.2 and 0.3 mol/ℓ) of) were prepared by dissolving (1.389, 2.315,3.241 g) of $NH_4F$ in a 250 ml of distilled water to achieve Fluorine high doping. The (Zn/F) ratio in the solutions was 1:1 as optimum high concentration ratio. The microscope

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http://dx.doi.org/10.1016/j.surfin.2017.06.003
Received 13 March 2017; Received in revised form 29 May 2017; Accepted 13 June 2017
Available online 15 June 2017

glass slides substrates were cleaned by ultrasonic cleaner for 15 minute using organic solvents. The substrate temperature was fixed at 450 °C whereas the spray rate was usually in the range of 2 ml/ min. The carrier gas pressure flow was about 0.3 bar Each spraying period lasts for around (15 sec) followed by around (3 min) waiting period to avoid excessive cooling of the hot substrates caused by the spraying process. The equation of the chemical reaction for preparing ZnO thin film is as follows:

$$ZnCl_2 + H_2O \xrightarrow{450^{\circ}} ZnO\downarrow + 2HCl\uparrow$$

The structure properties of (ZO and FZO) thin films were studied by X-ray diffraction XRD using Shimadzu (XRD - 6000) x-ray diffractometer with Cu–Kα (λ = 1.5404 Å) operating at 30 mA and 40 kV. The surface morphology of the prepared films was studied by scanning electron microscopy (SEM) (INSPECT-550). The optical properties of ZnO and ZnO:F thin films in the wavelength range (190–1100) nm have been investigated by using UV-VIS spectrophotometer type Shimadzu (UV-1650).

## Results and discussion

### *Structure properties*

Structural properties of the spray deposited ZO (Zinc Oxide) and FZO (Fluorine Zinc oxide) thin films were determined by XRD analysis. The x-ray diffraction pattern of ZnO and ZnO:F thin films with different fluorine doping concentrations was shown in Fig. 1. The results demonstrated that the films have a polycrystalline structure, with Hexagonal wurtize phase of ZnO. The figure shows that the pure and F doped ZnO films have a preferential orientation along (002) direction and the crystallites were highly oriented with the c-axes which was perpendicular to the substrate plane. The measured and standard from the (JCPDS) data (card no.36–1451) d-values are shown in Table 1. The wurtize crystal structure does not affected by the increasing of fluorine dopant concentration, where the existence of other peaks such as (102), (101) and (100) were also been detected but with lower intensities. Therefore F introduction in the lattice was by the substitution of $O^{-2}$ ions by F ions [16]. The intensity of the preferential orientation peak decreases with the increasing of fluorine doping levels which can be attributed to the lattice deformation caused by the defects which produced by the impurities sites. These results are in good agreement with previous works done by [9,16–18].

The lattice parameters (a) and (c) for pure and fluorine doped ZnO thin films were calculated from the following equation [19]:

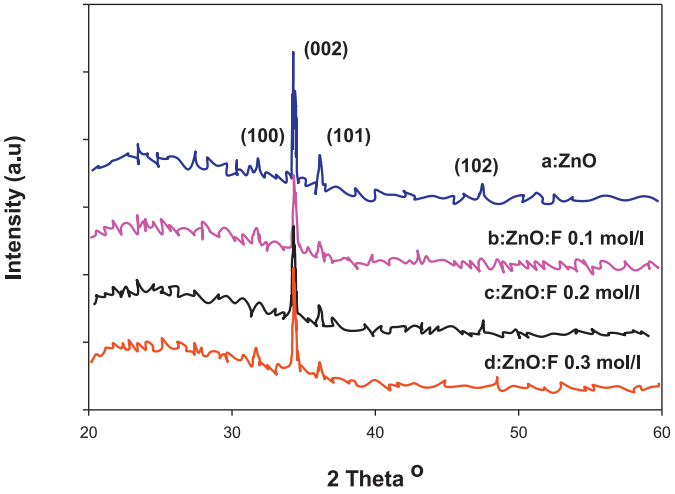


**Fig. 1.** XRD pattern of ZnO and ZnO:F thin films.

**Table 1**
The X-ray diffraction data analysis of ZnO and ZnO:F thin films.

| No. | Compound | d(Å) observed | d(Å) standard | (hkl) | a (Å) | c(Å) | Average grain size (nm) |
|---|---|---|---|---|---|---|---|
| 1 | ZnO (Pure) | 2.612 | 2.6033 | (002) | 3.236 | 5.224 | 39.541 |
| | | 2.466 | 2.4759 | (101) | | | |
| | | 1.916 | 1.9111 | (102) | | | |
| 2 | ZnO:F (0.1 mol/l F) | 2.828 | 2.8143 | (100) | 3.265 | 5.208 | 45.513 |
| | | 2.604 | 2.6033 | (002) | | | |
| | | 2.472 | 2.4759 | (101) | | | |
| | | 1.916 | 1.9111 | (102) | | | |
| 3 | ZnO:F (0.2 mol/l F) | 2.604 | 2.597 | (002) | 3.276 | 5.195 | 51.840 |
| | | 2.472 | 2.4759 | (101) | | | |
| | | 1.916 | 1.9111 | (102) | | | |
| 4 | ZnO:F (0.3 mol/l F)) | 2.828 | 2.8143 | (100) | 3.284 | 5.178 | 5.209 |
| | | 2.597 | 2.6033 | (002) | | | |
| | | 2.472 | 2.4759 | (101) | | | |

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Where d is the interplanar spacing of given Miller indices h,k and l. (a) and (c) values were in a good agreement with the (JCPDS) card data and shown in Table 1.

The average grain size has been determined by using the Scherrer's formula [20]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (2)$$

Where λ is the wavelength of the x-ray, θ is Bragg angle and B is the FWHM (full width at half maximum) value in radian. The values of the average grain size are included within the nano scale and confirm the nanostructure property of the as deposited and doped thin films as shown in Table 1.

The dislocation density δ of pure and Fluorine doped ZnO thin films is defined as the number of dislocation lines per unit volume and determined from the relation [21,22]:

$$\delta = \frac{1}{(D)^2} \quad (3)$$

The number of crystallites per unit surface area (N) could be calculated according to [21,22]:

$$N = \frac{t}{(D)^3} \quad (4)$$

Where t is the thickness of the films which were measured using gravimetric method and its values about 125 nm. Fig. 2 shows δ and N as a function of fluorine dopant concentration, it is absorbed that N has the same behavior of δ were they decreasing with average grain size and with the increasing of F concentration. The values of calculated δ and N with respect to the F concentration shown in Table 2.

The strain S directly depends on the constant $C_{XRD}$ and its value is related to the shift from the ASTM standard value, and determined using the equation [23]:

$$S = \frac{|c_{ASTM} - c_{XRD}|}{c_{ASTM}} \times 100\% \quad (5)$$

Where $c_{ASTM}$ is the c-lattice constant according to the ASTM card and $c_{XRD}$ is that measured from XRD pattern. When the lattice constant values vary from its $C_{ASTM}$ value which indicates that there is a positive (tensile) or negative (compressive) strain depending on the deposition conditions. The results showed that the strain value of pure ZnO thin film is (−0.334%) and increase to 0.5494% with the increase of F