The Crystalline Structure, Optical and Conductivity Properties of Fluorine Doped ZnO Nanoparticles

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This paper reports the effect of fluorine doping on ZnO thin films. Undoped and doped films were deposited by spray pyrolysis method on heated glass substrates at 380 °C with different concentrations of fluorine (0-15 at. %). X-ray diffraction patterns show the polycrystalline nature of the films with the preferred orientation along the *c*-axis. No other fluorine metal cluster and impurity phases have been observed with F doping. The crystalline size of the deposited thin films was calculated using Debye- Scherrer formula and found in the range between 13.7 and 37.3 nm. The optical transmittance of F doped ZnO thin films reduces up to 79 % as compared to undoped ZnO thin film in the visible region. The band gap was found to be decreasing in the range of 3.38-3.26 eV with F doping whereas it increases for higher doping of F concentration from 7-15 at. %. The Urbach energy (disorder) decreases from 120 to 90 meV that allows the atoms find a good site that is to say a better organization of the ZnO film, i.e. layers become homogeneous and well crystallized. The four-point techniques for measuring electrical conductivity show that all samples are n-type, and the best value of the electrical conductivity $9.24 \ 10^{-5} \ (\Omega \cdot cm)^{-1}$ was obtained for 5 at. % F. The increase of the electrical conductivity can be explained by the increase in carrier concentration of the films. FZO can be applied in different electronic and optoelectronic applications due to its high band gap, high transparency and good electrical conductivity.

Keywords: Spray pyrolysis, ZnO thin films, F-doped ZnO, Four-point techniques, Band gap, Conductivity.

1. INTRODUCTION

Transparent conducting oxides are promising materials in the class of optoelectronic devices due to their potential applications in gas sensors, piezoelectric transducers, light emitting devices and in solar cells [1]. Transparent oxide ZnO is a n-type semiconductor, has a direct band gap of 3-3.37 eV and a large exciton binding energy of 60 meV more than the thermal energy at room temperature [2]. ZnO is widely used because of its properties, nontoxic, less expensive and abundantly available on earth, chemically and thermally stable [1, 3]. There are quite similarities between the optical properties and band structures of ZnO and GaN [4]. Both GaN and ZnO are direct wide band gap ($E_g > 3$ eV) semiconductors, transparent in the visible region, having wurtzite crystal structure, comparable lattice constants, with nearly the same c/a lattice constant ratios [5]. Doping is a widely used method to improve physical properties of semiconductor compounds [6]. These properties can be greatly influenced by the chemical doping or formed intrinsic lattice defects. As well as dopant concentration, it is well known that the physical properties of ZnO films also depend on the preparation technique, source material and growth temperature. ZnO thin films can be grown by various methods such as thermal evaporation, chemical vapor deposition, sol gel method, electrochemical deposition, magnetron sputtering deposition, and spray pyrolysis [7, 8].

Among these methods, the simple and inexpensive spray pyrolysis method allows easy control over deposition parameters as well as reproducibility [9]. The aim of this paper is to study the effect of fluorine doping on the structural, optical and electrical behavior of undoped ZnO, FZO thin films synthesized on glass substrates by spray pyrolysis method; and the properties of these films were studied and discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Samples

ZnO:F (0-15 at. %) thin films were prepared on corning glass substrates using spray pyrolysis technique. In this procedure, to prepare 0.2 M solution of undoped ZnO, zinc acetate dehydrate $[C_4H_6O_4Zn.2H_2O]$ was dissolved in distilled water. The solution was kept under constant stirring for about 2 hours. For doping, appropriate amount of ammonium fluoride (HN_4F) and zinc acetate was dissolved in 100 ml of distilled water and stirred for 2 hours to transparancy solution. Before deposition of the films, the corning glass substrates were dipped in a mixture of distilled (DI) water and HCl, then cleaned ultrasonically followed by acetone and with DI water for 10 min, respectively. After drying the substrates, the films were deposited by spray pyrolysis with the value of pressure and the nozzle-substrate distance of 2 bars and 20 cm, respectively. The films were then preheated on a hot plate at 380 °C for the evaporation of organic solvents. To keep the substrate temperature constant, the pre-cursor solution was deposited cyclically, 10 s of spraying followed by 45 s without spraying. Undoped ZnO was used as a

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reference sample. The F content was varied as 5, 7 and 15 at. %. The F content in the starting solution is referred here as the atomic percentage with respect to Zn.

2.2 Devices and Measurements

The crystal structure of ZnO thin film was determined by X-ray diffraction (XRD) using diffractometer with Cu-Kα X-ray source. The optical transmission spectra are used to study the optical properties of deposited thin films and have been analyzed using UV-Visible spectrophotometer at room temperature. The electrical conductivity was measured with the four-point techniques.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Fig. 1 shows the XRD spectra of ZnO:F thin films prepared on corning glass substrates in the 2θ range of 25-60°. The diffraction peaks are indexed by comparing the data with JCPDS of card number (36-1451). It has been observed that the films are polycrystalline in nature, having (002) orientation along the c-axis perpendicular to the substrate surface. The three major peaks at 31.8°, 34.5° and 36.4° corresponding to (100), (002) and (101) orientations of ZnO have been observed in all the samples. It is to be noted that, the (002) peak intensities of the ZnO films are found to increase with increasing F concentration. Similarly, G.H. Kim and et al. [10] have observed that the (002) peak intensity appeared to increase as the fluorine content increased.

The full width at half maxima of the (002) peak of all the samples was obtained by the Lorentzian fitting tool. The grain size (D) corresponding to (002) peak was calculated by the Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \qquad (1)$$

where λ is the X-ray wavelength of Cu-K_α (1.54046 Å), θ is the diffraction angle (in radians) and β is the full width at half maximum of the peak. According to hexagonal symmetry, the lattice constant can be calculated from the following equation:

$$\frac{1}{d^2} = \frac{4}{3a^2}\left(h^2 + hk + k^2\right) + \frac{l^2}{c^2}, \qquad (2)$$

where d is the interplanar spacing, h, k, l are the crystal plane indices and a, b, c are the cell parameters.

The biaxial stress along the c-axis was calculated using the relation [11]

$$s = 453.6 \times 10^2 \left[\left(c - c_0\right)/c\right]. \qquad (3)$$

The lattice strain (ε) is calculated using the relation [12]

$$\varepsilon = \frac{\beta \cos\theta}{4}, \qquad (4)$$

where the lattice parameter of the strained films was obtained from the XRD data, and c_0 is the strain free lat-

tice parameter ($c_0 = 0.5206$ nm). The values of dislocation densities (δ) are calculated using the relation [13, 14]
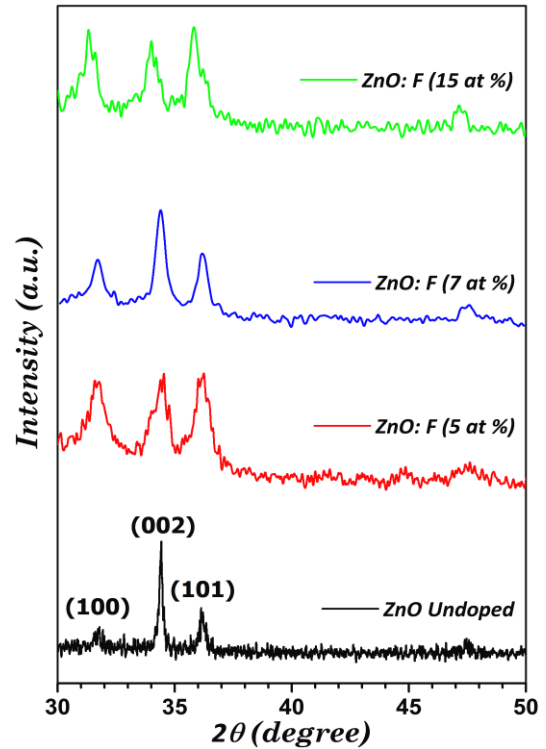
$$\delta = \frac{1}{D^2}. \qquad (5)$$

Fig. 1 – XRD patterns of FZO sprayed thin films

3.2 Optical Properties

Fig. 2 shows the transmission and absorption spectra of the sprayed FZO thin films in the wavelength range of 300-800 nm. It is observed that the transmission is about 80 % for undoped sample and decreases slightly with the increase in doping concentration. This is due to the decrease in the grain size (see Table 1) leading to the higher density of grain boundaries, that can be explained by the atomic radius between Zn and F, which in turn leads to a decrease in transmission [15].
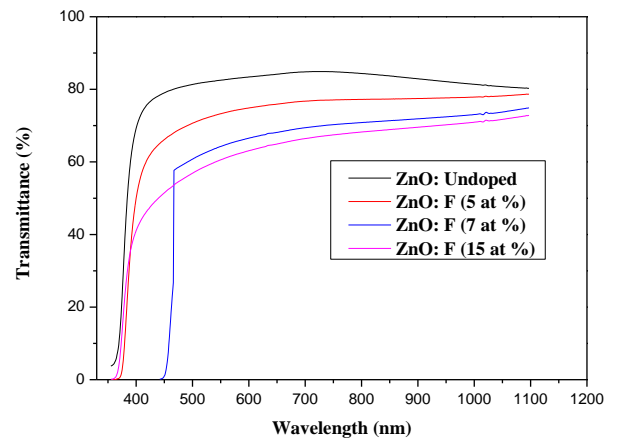

Fig. 2 – Transmission spectra for undoped and F-doped (0, 5, 7 and 15 at. %) ZnO films prepared at 380 °C

Table 1 – Various structural parameters of FZO sprayed thin films

Samples	Grain size D, nm	dislocation densities δ, cm^{-2}	Cell parameter, Å		lattice strain ε, %
			$a = b$	c	
Undoped ZnO	37.27	7.20E+10	3.258	5.208	0.404
ZnO:F (5 at. %)	13.7	5.33E+11	3.259	5.211	0.827
ZnO:F (7 at. %)	23.85	1.76E+11	3.260	5.219	0.493
ZnO:F (15 at. %)	20.7	2.33E+11	3.283	5.267	0.582

In Fig. 3, we observe what are called localized states formed in band tails at the boundaries of the band gap, the valence and conduction bands. For energies greater than E_c and less than E_v, the extended states are found (Fig. 5), this difference is known as disorder. When the disorder becomes too great (e.g. with the appearance of hanging bonds or impurities in the material), the tails may become entangled. We will then define the notion of Urbach parameter (E_{00}) which corresponds to transitions between the extended states of the valence band and the localized states of the conduction band. The absorption coefficient is linked to disorder by the law [16]:

$$\alpha = \alpha_0 \exp(h\nu / E_{00}) , \qquad (6)$$

E_{00} being the width of the tape tail that characterizes the disorder.

The optical band gap values (E_g) are determined by using the relation [16]:

$$(\alpha h\nu)^2 = A\left[h\nu - E_g\right], \qquad (7)$$

where A is a constant, which is different for different transitions, h is the Planck constant, ν is the frequency of incident light, and E_g is the corresponding band gap.
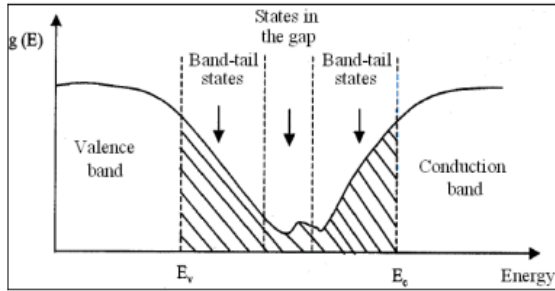
Fig. 3 – Distribution function of the energy states in the bands

From Fig. 4, the band gap values are determined as a function of fluorine concentrations by extrapolating the straight line portion of the $(\alpha h\nu)^2$ versus $(h\nu)$ variation to $(\alpha h\nu)^2 = 0$. The obtained values ranging from 0 to 15 at. % are: 3.38 eV (ZnO), 3.37 eV (Zn0.98 F0.02), 3.28 eV (Zn0.95 F0.05), 3.26 eV (Zn0.93 F0.07), 3.32 eV (Zn0.85 F0.15O). The band gaps generally decrease due to the band shrinkage effect with increasing carrier concentration [17]. The value of E_g for ZnO thin film was found to be decreased from 3.38 to 3.32 eV with increase in F doping concentration. The decrease in the band gap can be attributed to the strong sp-d exchange interaction between the band electrons and localized electrons of the dopant.

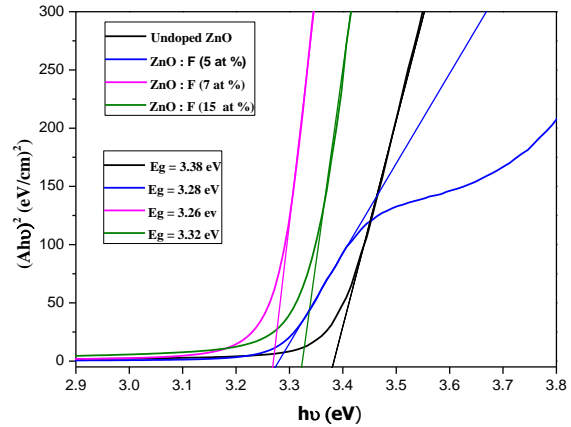These results indicate that the optical properties of ZnO films are affected by fluorine doping.

Fig. 4 – Plots of $(\alpha h\nu)^2$ versus $h\nu$ for Zn:F films with different values of fluorine concentration
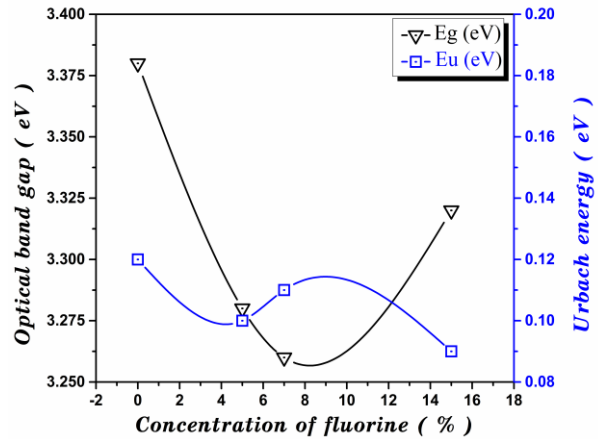
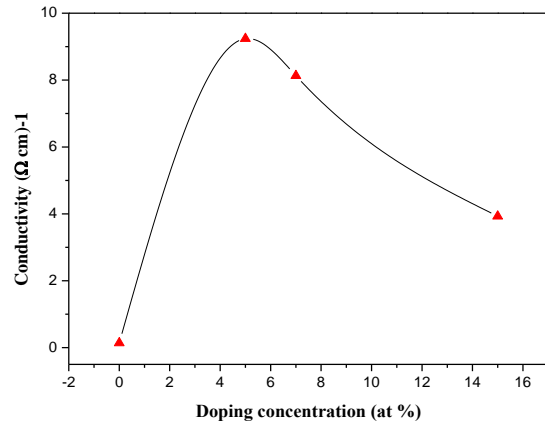**Fig. 5** – Variation of the optical gap and Urbach energy of FZO films

Fig. 6 – The electrical conductivity of FZO thin films deposited at various fluorine concentrations, such as ($x = 0$; 5; 7; 15 at. %)

3.3 Electrical Properties

Fig. 6 shows the variation of the electrical conductivity of ZnO thin films doped with fluorine measured by four-point techniques at room temperature for the films deposited at various x concentrations, such as (x= 0; 5; 7; 15 at. %). The electrical conductivity of the samples increases with the increase of the fluorine concentration from 0 to 5 at. % and reaches its maximum value of 9.24 10^{-5} $(\Omega \cdot cm)^{-1}$ at a concentration of 5 at. % of the fluorine. That is due to the reduction of charge carrier loss to crystalline defects and grain boundaries, which increases carrier mobility. The latter is due to a decrease in the resistivity to the movement of the charges.

4. CONCLUSIONS

FZO thin films with wurtzite structure have been successfully grown on corning glass substrates by low cost spray pyrolysis process. The XRD results revealed that FZO films are polycrystalline in nature with highly c-axis preferred orientation along (002) plane and presented a hexagonal crystal structure. Due to fluorine doping, the crystallite size decreases from 37.27 to

20.7 nm.

The average optical transmittance for ZnO is above 80 % in the visible region, and it reduces for FZO thin films and the optical band gap value decreases from 3.38 to 3.32 eV as doping concentration increases. The optical and electrical studies clearly indicate the presence of fluorine in ZnO. Hence, the observed decrease in the optical band gap and the variation in the electrical conductivity could be directly attributed to the effect of F ion incorporation into ZnO lattice. At 5 at. % of F doping, the film has the highest conductivity equal to $9.24 \cdot 10^{-5}$ $(\Omega \cdot cm)^{-1}$. These FZO films may be used for photovoltaic devices.

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Кристалічна структура, оптичні та провідні властивості наночастинок ZnO, легованих фтором

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У роботі вивчений вплив легування фтором на властивості тонких плівок ZnO. Нелеговані і леговані плівки осаджували методом спрей-піролізу на нагріті скляні підкладки при 380 °C з різними концентраціями фтору (0-15 ат. %). Рентгенівські дифрактограми показують полікристалічну природу плівок з переважною орієнтацією вздовж осі *c*. Ніякі інші кластери та домішкові фази не спостерігалися при легуванні фтором. Розмір кристалітів осаджених тонких плівок розраховувався за допомогою формули Дебая-Шеррера і знаходився в діапазоні від 13,7 до 37,3 нм. Оптичне пропускання тонких плівок ZnO, легованих фтором, зменшується до 79 % порівняно з нелегованою тонкою плівкою ZnO у видимій області. Встановлено, що ширина забороненої зони зменшується в діапазоні 3,38-3,26 еВ при легуванні фтором і збільшується для більш високої концентрації фтору з 7-15 ат. %. Енергія Урбаха (розупорядкування) зменшується із 120 до 90 меВ, що дозволяє реалізувати кращу органі-

зацію плівки ZnO, тобто шари стають однорідними і добре кристалізуються. Чотириточкові методи вимірювання електропровідності показують, що усі зразки мають n-тип, а найкраще значення електропровідності $9,24 \cdot 10^{-5}$ (Ω см)$^{-1}$ отримано за концентрації фтору 5 ат. %. Збільшення електропровідності можна пояснити збільшенням концентрації носіїв у плівках. FZO може бути застосований в різних електронних і оптоелектронних додатках завдяки великій забороненій зоні, високій прозорості і гарній електропровідності.

Ключові слова: Спрей-піроліз, Тонкі плівки ZnO, ZnO легований F, Чотириточкові методи, Заборонена зона, Провідність.