Effect of fluorine (F) on structural and electrical properties of sprayed ZnO thin films

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Abstract. Un-doped and F doped ZnO thin films have been deposited on glass substrate using spray pyrolysis technique at substrate temperature 350 °C. The structural and electrical properties of these films were investigated by X-ray diffraction (XRD) and Van der Pauw method. Electrical transport study confirms semiconducting nature of the films. Dopant F atom enhances electrical conductivity substantially with the increase of F content. Activation energy measurement confirms that electrical transport mainly occurs due to free carrier transition and free excitation of defect states to the conduction band. The carrier concentration of ZnO increases with F-doping as confirmed by Hall voltage measurement and the order of carrier concentration is $10^{19}$ cm$^{-3}$.

1. Introduction

Zinc oxide (ZnO) is the most important semiconductor material suitable for microelectronic and shortwave optoelectronic applications owing to its high conductivity, chemical stability, nontoxicity and transparency, as well as being inexpensive and abundance in nature. ZnO is a type II-VI direct band gap (3.37 eV) semiconductor with high excitonic binding energy (60 meV at RT) exhibiting near UV emission [1-3]. Recently, ZnO with hexagonal Wurzite crystal structure has been extensively investigated as an alternative material to ITO used in transparent electrodes, window materials in solar cells, light emitting diodes, flat panel displays, sensors etc. [4-8]. Zinc oxide thin films have attracted more attention due to their broad range of applications such as window layer in solar cells, piezoelectric nano-generators, photo detectors, surface acoustic wave device, gas sensors, biomedicine etc. [9-11].

Most of the researchers reported the effect of divalent and trivalent cation dopants on doped ZnO thin films. However, a few studies on F doped ZnO are found in the literature despite the fact that F can be an adequate anion doping candidate due to its similar ionic radius to the oxygen (F$^-$: 0.136 nm, O$^{2-}$: 0.132 nm) [12, 13]. It is well known that in semiconductor, carriers can be originated from intrinsic donors and from extrinsic doping. In ZnO lattice intrinsic donors are oxygen vacancies present (if any) and Zn$^{2+}$ atoms. On the other hand, extrinsic doping is substitution of F$^-$ for O$^{2-}$ which will liberate one free electron for each F$^-$ substitution for O$^{2-}$ and acts as a donor. Furthermore, when oxygen is replaced by fluorine in ZnO, it may passivate surface dangling bond resulting in reduction of carrier trapping. As a result, overall carrier concentration will be enhanced and contribute to electrical conduction. Therefore, F doped ZnO with high optical transparency can be used as an electrode or window layer for solar cell fabrication. Motivated with the fact described above, present study has been designed.

In the last few years, variety of deposition techniques have been employed to fabricate the ZnO thin films; including (RF) magnetron sputtering, sol gel, chemical vapor deposition, pulsed laser deposition...
and chemical spray pyrolysis etc. [14-19]. Among all these deposition techniques, the chemical spray pyrolysis (SP) is very simple, versatile and relatively cost-effective processing technique having the capability to produce large area, high quality adherent films of uniform thickness. The main focus of this work is to study the effect of F concentration on the microstructure and electrical transport properties of ZnO films and discussed.

2. Experimental

Un-doped and F doped ZnO films have been deposited on ordinary glass substrate by spray pyrolysis technique at substrate temperature 350 °C in air ambient. A homogeneous solution was prepared by dissolving zinc acetate dihydrate ((CH₃COO)₂Zn.2H₂O) and ammonium fluoride (NH₄F) in distilled water at room temperature. The solution was sprayed through a commercially available medical infusion pipe onto the heated substrate by an air compressor. The glass substrates were cleaned by using liquid detergent, distilled water, piranha solution, ethanol and again distilled water. The cleaned substrate was placed on a substrate holder and heated by a simple electric heater. The temperature was controlled through a copper-constantan thermocouple. In preparation of all the films the distance between tip of the spray nozzle and the surface of the substrate was kept at 20 cm, the rate of solution flow was 0.30 ml/min for half an hour and substrate temperature was 350 °C. The conditions for film deposition were kept constant so that thicknesses were same for all samples. The thicknesses of the films were (150 ±10) nm measured by Newton’s ring method. Details of the film preparation by SP technique have been given elsewhere [20]. The chemical reactions that take place on the heated substrate are as follows:

\[(\text{CH}_3\text{COO})_2\text{Zn}.2\text{H}_2\text{O} \xrightarrow{350 ^\circ\text{C}} \text{ZnO} + \text{CO}_2(\text{g}) + \text{CH}_4(\text{g}) + \text{Steam (g)}\]

\[(\text{CH}_3\text{COO})_2\text{Zn}.2\text{H}_2\text{O} + \text{NH}_4\text{F} \xrightarrow{350 ^\circ\text{C}} \text{ZnO}:\text{F} + \text{CO}_2(\text{g}) + \text{NO (g)} + \text{CH}_4(\text{g}) + \text{Steam (g)}\]

X-ray diffraction (XRD) study was performed using X-ray diffractometer, (D2 PHASER, BRUKER) with monochromatic CuKα radiation of wavelength, λ = 0.1542 nm operated at accelerating voltage 30 kV and current 10 mA. X-ray diffraction patterns of the films were recorded by varying diffraction angle 2θ from 20˚ to 80˚. Electrical resistivity and Hall voltage measurements were carried out by van der Pauw method [21].

3. Results and discussion

Figure 1 shows the XRD patterns of un-doped and F doped ZnO thin films deposited at 350 °C substrate temperature using spray pyrolysis technique indicating hexagonal Wurtzite crystal structure of the films. All the films have seven diffraction peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) planes, which indicates the polycrystalline nature of ZnO films. No extra peaks other than ZnO were observed. So, F atoms may be substituted O atoms or incorporated into interstitial sites in the ZnO lattice confirming the monophasic (ZnO) character of the grown films. The peak intensity of the films is different depending on the amount of F dopant. As seen from figure, the diffraction angle of all the peaks shift towards lower angle results in increase in a and c lattice parameters as given in table 1.

The crystallite size, ξ was estimated using Debye-Scherrer formula [22],

\[\xi = \frac{0.94\lambda}{\beta\cos\theta}\]

(1)

where \(\lambda\) is the incident X-ray wavelength and \(\beta\) is the full-width at half maximum of the diffraction peak. The corresponding lattice parameters were calculated using the formula [23],

\[\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + l^2}{a^2}\right) + \frac{l^2}{c^2}\]

(2)
It is observed that for all the films lattice parameters $a$ and $c$ increased indicating the substitution of F atoms at the O sites, because of the difference of electronegativity between F and O ions. Each substitution of O atom by F atom gives one free electron in the system. However, observed intensity diminution in 2, 3 and 5% F doped samples may be due to incorporation of F atoms in the interstitial positions of host lattice.

The lattice strain affects the crystal structures and properties of ZnO thin films to some extent and was calculated for (100) and (002) peaks using the formula,

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$  \hspace{1cm} (3)

The dislocation density represents the total length of dislocation lines per unit volume of the crystal. The dislocation density, $\delta$ for two major peaks (100) and (002) of all the samples were estimated using the Williamson and Smallmans relation [24],

$$\delta = \frac{1}{\xi^2}$$  \hspace{1cm} (4)

The calculated lattice strain and dislocation density of all the films are tabulated in table 1.

Figure 1. The XRD pattern of the un-doped and F doped ZnO thin films.
Table 1. Structural and defect parameters of un-doped and F doped ZnO films.

| F conc. in ZnO (mol%) | Lattice parameter (nm) | Crystallite size, \( \xi \) (nm) | Lattice strain, \( \epsilon \times 10^{-3} \) | Dislocation density, \( \delta \times 10^{15} \) lines/m² | c/a ratio |
|------------------------|------------------------|-------------------------------|-----------------------------|--------------------------|----------|
|                        | \( a \) | \( c \) | (100) | (002) | (100) | (002) | (100) | (002) |
| 0                      | 0.3154 | 0.5076 | 27   | 18  | 4.6714 | 6.4106 | 1.3717 | 3.0864 | 1.6089 |
| 1                      | 0.3188 | 0.5131 | 55   | 20  | 6.4970 | 5.9933 | 3.3058 | 2.5000 | 1.6094 |
| 2                      | 0.3199 | 0.5135 | 18   | 14  | 1.8668 | 2.2528 | 3.0864 | 5.1020 | 1.6052 |
| 3                      | 0.3216 | 0.5171 | 44   | 36  | 2.9809 | 3.2990 | 0.5165 | 0.7716 | 1.6079 |
| 5                      | 0.3220 | 0.5156 | 37   | 36  | 3.5831 | 0.7035 | 0.7035 | 0.7716 | 1.6012 |

Figure 2 shows the plot of electrical resistivity as a function of temperature for un-doped and F doped ZnO thin films. The resistivity found to decrease with the increase of temperature which confirms the semiconducting behaviour of ZnO films. This effect may be due to increase of transition of donor electrons to conduction band. It can also be seen that resistivity is strongly influenced by the doping and it decreases with F doping concentration. The RT resistivity for un-doped ZnO film is about 6.979 \times 10^{-2} (\Omega \cdot \text{cm}) and it decreases to 5.939 \times 10^{-2} (\Omega \cdot \text{cm}) for 5% F doped sample.

Figure 3 illustrates the variation of RT resistivity (\( \rho \)), carrier concentration (\( n \)) and Hall mobility (\( \mu_H \)) as a function of F concentration. As the F content increases, carrier concentration of the films increases while RT resistivity and mobility decrease.
The highest carrier concentration is about $1.2 \times 10^{19}$ (cm$^{-3}$) for un-doped sample and it increases up to $5.1 \times 10^{19}$ (cm$^{-3}$) for 5% F doped ZnO sample. On the other hand, highest mobility is found for undoped sample. The resistivity of as deposited F doped ZnO films obtained in this study is found consistent with the resistivity of F doped ZnO film prepared by magnetron sputtering (as-grown) [25] and chemical spray [26] technique but higher than that of pulsed laser deposition method [27] as illustrated in table 2. The carrier concentration and mobility were also found to consistent [25]. However, after vacuum annealing of magnetron sputtered sample, they found lower resistivity, higher carrier concentration and mobility [25] as given in table 2. Wang et al [14] also found lower resistivity with higher carrier concentration and mobility by increasing substrate temperature from RT to 300 °C. In general, carrier mobility become lower if crystal grain size is small. Although, the crystallite size of undoped and F doped films is found moderate in this study, however, mobility found to decrease with increasing F content. This is because, a part of free carriers may be trapped by surface dangling bonds and decrease mobility [28].

The activation energy $\Delta E$ can be calculated using the relation,

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2K_BT}\right)$$  \hspace{1cm} (5)

where, $\sigma_0$ is a constant and $\sigma$ is the electrical conductivity, $K_B$ is the Boltzmann constant and T is the absolute temperature. For the calculation of activation energy, the logarithmic variation of electrical conductivity with $1/T$ was taken for un-doped and F doped ZnO thin films as illustrated in figure 4. The activation energies of all the films were calculated from the slopes of the curves in the temperature range 303 K to 358 K ($\Delta E_1$) and 358 K to 453 K ($\Delta E_2$).
Table 2. RT resistivity (ρ), carrier concentration (n) and Hall mobility (μ_H) of un-doped and F doped ZnO films.

| Preparation technique and conditions | F conc. in ZnO (mol%) | Resistivity, at (RT) ρ ×10⁻² (Ω-cm) | Carrier concentration n ×10¹⁹ (cm⁻³) | Hall mobility, μ_H (cm²/Vs) | Ref. |
|-------------------------------------|-----------------------|--------------------------------------|--------------------------------------|-----------------------------|-----|
| Spray 350 °C, air ambient           | 0                     | 6.979                                | 1.2                                  | 7.88                        | this work |
|                                     | 1                     | 6.768                                | 2.0                                  | 4.52                        |     |
|                                     | 2                     | 6.568                                | 3.4                                  | 2.79                        |     |
|                                     | 3                     | 6.243                                | 4.1                                  | 2.45                        |     |
|                                     | 5                     | 5.939                                | 5.1                                  | 2.05                        |     |
| Magnetron sputtering 150 °C         | As-grown              | 7.84                                 | 1.7                                  | 4.7                         | [25] |
|                                     | Vacuum annealed       | 0.36                                 | 5.6                                  | 30.5                        |     |
| Chemical spray 300 °C               |                       | 6.83                                 | -                                    | -                           | [26] |
| Pulsed laser                        |                       | 0.051                                | 50.27                                | 23                          | [27] |

Thus more charge carriers overcome the activation energy barrier causing the electrical conduction. In the higher temperature region, the trapped charge carriers induce the electrical conduction at the grain boundaries with donor electron. Thus with the increase of temperature, the conduction mechanism changes from only thermally activated charge carriers to the grain boundary trapped charge conduction mechanism. The ΔE₁ and ΔE₂ values are tabulated in table 3.

Figure 4. Variation of lnσ with 1000/T for un-doped and F doped ZnO thin films.
Table 3. Activation energy of un-doped and F doped ZnO thin films.

| F conc. in ZnO (mol%) | Activation energy, $\Delta E$ (eV) |
|-----------------------|-----------------------------------|
|                       | $\Delta E_1$ (303-358) K          | $\Delta E_2$ (358-453) K |
| 0                     | 0.0115                            | 0.0147                     |
| 1                     | 0.0105                            | 0.0135                     |
| 2                     | 0.0062                            | 0.0103                     |
| 3                     | 0.0089                            | 0.0135                     |
| 5                     | 0.0095                            | 0.0121                     |

In the low temperature region, $\Delta E_1$ varies from (0.0062 - 0.0115) eV and in the high temperature region, $\Delta E_2$ varies from (0.0103 - 0.0147) eV, though these variations are inconsistent with doping concentration of F. In the lower temperature region, as the temperature is increased, the electrons are excited thermally from donor levels to conduction band.

4. Conclusions
Un-doped and F doped ZnO thin films were deposited on glass substrate at 350 °C by spray pyrolysis technique. XRD characterization of all the films revealed polycrystalline nature. Hall measurement reveals un-doped and F doped ZnO films are n-type semiconductor and the effective carrier concentrations are found to be the order of $\sim 10^{19}$ cm$^{-3}$ and Hall mobility as high as 7.88 cm$^2$/Vs.

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