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Full Length Research Paper

Effects of fluorine incorporation on the microstructure and optical properties of ZnO thin films synthesized by Sol-gel technique

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Fluorine doped Zinc oxide (ZnO) [FZO] transparent conducting thin films were deposited by sol-gel spin coating method. Zinc acetate and amonium fluoride were used as precursor solution materials. Microstructural, morphologycal, and optical properties of the films were investigated as a function of flourine (F) doping ranging from 0 to 3.5% mole. From x-ray diffraction (XRD) patterns the films exhibited a hexagonal wurtzite structure with preferred c-axis orientation. All the films had a highly preferential c-axis orientation and exhibited (002) preferential growth in all the dopant ratios. Grain sizes of the films were varied in range of 15 to 18 nm. The SEM images of the films showed well crystallinity with good homogeneity, smooth surface and uniform grains. The average optical transmittance in the entire visible wavelength region was higher than 95% for all F-doped ZnO except undoped ZnO thin film. The band gap energy values were determined as 3.270, 3.291, 3.293 and 3,287 eV, respectively for undoped ZnO, 0.5, 1.5 and 3.5% mole FZO samples. The band gap values increased with increasing the F dopant concentration for all doped samples. These results make FZO thin films an attractive candidate for transparent material applications.

Key words: Flourine doped Zinc oxide (ZnO), Sol-gel growth, transparent conducting oxide (TCO), thin films, microstructures.

INTRODUCTION

Transparent conducting oxide (TCOs) thin films have attracted the attention of many researchers due to their wide applications in both science and technology. Different metal oxide semiconductors such as In_2O_3, SnO_2, ZnO and TiO_2 have been employed to fabricate TCO thin films (Cao et al., 2011). Among TCO materials, ZnO is one of the metal oxide semiconductors suitable for use in optoelectronic devices, varistors, sensors, piezoelectric nanogenerators, thin film solar cells (Pawar et al., 2008; Sanchez-Juarez et al., 1998) flat panel liquid crystal displays, light emitting diodes (Cao et al., 2011) due to its low material cost, abundance in nature, easy fabrication, non-toxicity, low electrical resistivity, good optical transparency in the visible region, direct band gap (3.37 eV) with a large excitation binding energy of 60 meV (Pawar et al., 2008; Sanchez-Juarez et al., 1998; Yoon et al., 2008) and high chemical stability (Biswal et al., 2010).

Pure ZnO is an n-type intrinsic semiconductor and it is difficult to control some properties. Therefore, in order to control or improve some properties of ZnO, many researchers focused on doping ZnO with anion and cation dopants such as Cerium (Ce), Fluorine (F), Erbium (Er), Aluminium (Al), Tin (Sn), Indium (In), Antimony (Sb), Gallium (Ga), Iron (Fe) etc. (Sofiani and Sahraoui, 2007; Choi et al., 2005; Maldonado et al., 2010; Zhang et al., 1999; Wen et al., 2010; Paraguay et al., 2000). Among

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these, fluorine (F) is one of anion dopants and its radius is similar to that of oxygen (F = 1.31 Å; O^{2-} = 1.38 Å) (Biswal et al., 2010). Therefore, it can be an adequate anion doping candidate due to lower lattice distortion compared to Al, Ga or In (Tsai et al., 2009).

Undoped and doped ZnO thin films have been prepared using various methods such as spray pyrolysis (Guillén-Santiago et al., 2004), electron beam evaporation (Xu et al., 2005), successive ionic layer adsorption and reaction (SILAR) (Sakthivelu et al., 2011), rf and dc magnetron sputtering (Zhang et al., 1999), pulsed laser deposition (PLD) (Wen et al., 2010), and sol-gel process (Maldonado et al., 2010; Ilican et al., 2008b; Shakti et al., 2010; Sagar et al., 2005; Ghodsi and Absalan, 2010; Rokn-Abadi et al., 2009; Bahadur et al., 2007). Among these techniques, the sol-gel is attractive candidate due to its easy manipulation of the samples and its ability to prepare high quality thin films in large scale. Among the other advantages of this technique are its simplicity, safety, low cost (Ghodsi and Absalan, 2010), high purity and homogeneous deposition at relatively low temperatures (Sagar et al., 2005; Rokn-Abadi et al., 2009), easy control of chemical components (Maldonado et al., 2010; Ilican et al., 2008a).

According to our knowledge, only a few studies on F-doped ZnO thin films by sol-gel have been reported in the litrerature (Maldonado et al., 2010; Ilican et al., 2008b). In the present study, we report the influence of the F doping on structural and optical properties of ZnO thin films prepared by sol-gel technique.

MATERIALS AND METHODS

Synthesis

ZnO thin films were deposited on glass substrates by spin coating sol-gel method. The coating precursor solution was prepared by using Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] as a starting material together with 2-Methoxyethanol ($C_3H_8O_2$) and Monoethanolamine (C_2H_7NO, MEA) were a solvent and stabilizer, respectively. For the FZO (ZnO:F) solution, the ammonium fluoride (NH_4F) was inserted into the solution to use as the fluorine source. The molar ratios of $Zn(CH_3COO)_2.2(H_2O)$ and metal dopant to MEA were maintained at 1:1. 0.5 M Zinc acetate dihydrate and 0.5 M ammonium fluoride were mixed in different solution mole ratios as 0.5, 1.5 and 3.5% mole F and the films were named as FZO-1, FZO-2, FZO-3, FZO-4 according to fluorine content, respectively, and undoped ZnO was used as a reference sample. The sol was stirred at 90°C for 8 h to obtain a clear and homogenous solution in balloon flask which is tightly sealed. The glass substrates were cleaned in acetone and methanol by using an ultrasonic cleaner and the substrates were immersed in diluted 10% HF (hydrofluoric acid) for 15 s. Then the substrates were rinsed with large amount of de-ionized (DI) water and dried with nitrogen. The resultant solution was dropped on glass substrate, which was rotated at a speed of 3000 rpm for 25 s by using a spin-coater. The as-coated film was sintered at 250°C for 5 min to evaporate solvent and remove the organic sediments and then spontaneously cooled to room temperature. This procedure was repeated for 10 times to obtain the intended thickness and film quality. The same procedure was repeated for the films prepared with different values of fluorine doped and finally, they were annealed in air at 450°C for 30 min.

Characterizations

Morphological properties of the films were determined with Nova Nanosem 430. The optical absorbance of the films were recorded in spectral region of 350 to 1100 nm at 300 K using a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 35) which works in the range of 200 to 1100 nm and has a wavelength accuracy of better than ±0.3 nm. X-ray diffraction (XRD) patterns were taken using a Rigaku D/Max-IIIC diffractometer. The diffractometer reflections were investigated at room temperature and the values of 2θ were altered between 20 and 90°. The incident wavelength was 1.5418 Å.

RESULTS AND DISCUSSION

The crystal structure and orientation of undoped and F-doped ZnO (FZO) thin films, which have different flourine concentrations, were investigated by X-ray diffraction (XRD) patterns. Figure 1 shows the XRD patterns of ZnO and FZO films deposited at different F dopant concentrations. These spectra indicate that the films have polycrystalline nature (JCPDS card file no. 36-1451) and a preferred orientation with the c-axis perpendicular to the substrates (Cao et al., 2011).

The dominant diffraction peak for the films was (002) line. In addition to the (002) peak, other peaks such as (100), (101), (102), (110), (103), (112) and (004) with comparatively lower intensities were also observed for the films (Yakuphanoglu et al., 2007; Gonzalez-Hernandez et al., 2010). When F was incorporated in the film, the intensity of the peak corresponding to the plane (002) fluctuated with doping concentrations, namely intensities of (002) peak the firstly decreased at for 1.5% mole F, then increased for 3.5% mole F and the intensities of other peaks continuously decreased with increasing F doping content. This result indicates that the inactive F atoms in the FZO films have been segregated into grain boundaries and to restrict the crystallization and preferred orientation of ZnO. Observed weak peaks for FZO films with increasing F content from 0.5 to 3.5% mole could be implied to these inactive F atoms. Similar results for AFZO (Al and F codoped ZnO) and AZO (Al doped ZnO) thin films has been studied by Choi et al. (2005).

Also, low intensity (222) peak for ZnF_2 (or NH_4ZnF_3) was appeared at 3.5% mole F doped ZnO (JPCDS card fine no. 07-0214). This is the indication of fluorine compounds involving extra phases such as ZnF_2. This can be explainded to high volatility of fluorine (Choi et al., 2005; Yakuphanoglu et al., 2007; Gonzalez-Hernandez et al., 2010; Tsai et al., 2010). The crystallinity of ZnO thin films was decreased with 1.5% mole F doping, then was increased at 3.5% mole. It is seen in Figure 1 that the crystallinity of ZnO thin films was deteriorated with highly fluorine incorporation (Yakuphanoglu et al., 2007). This deterioration can be lead to the formation of configuration

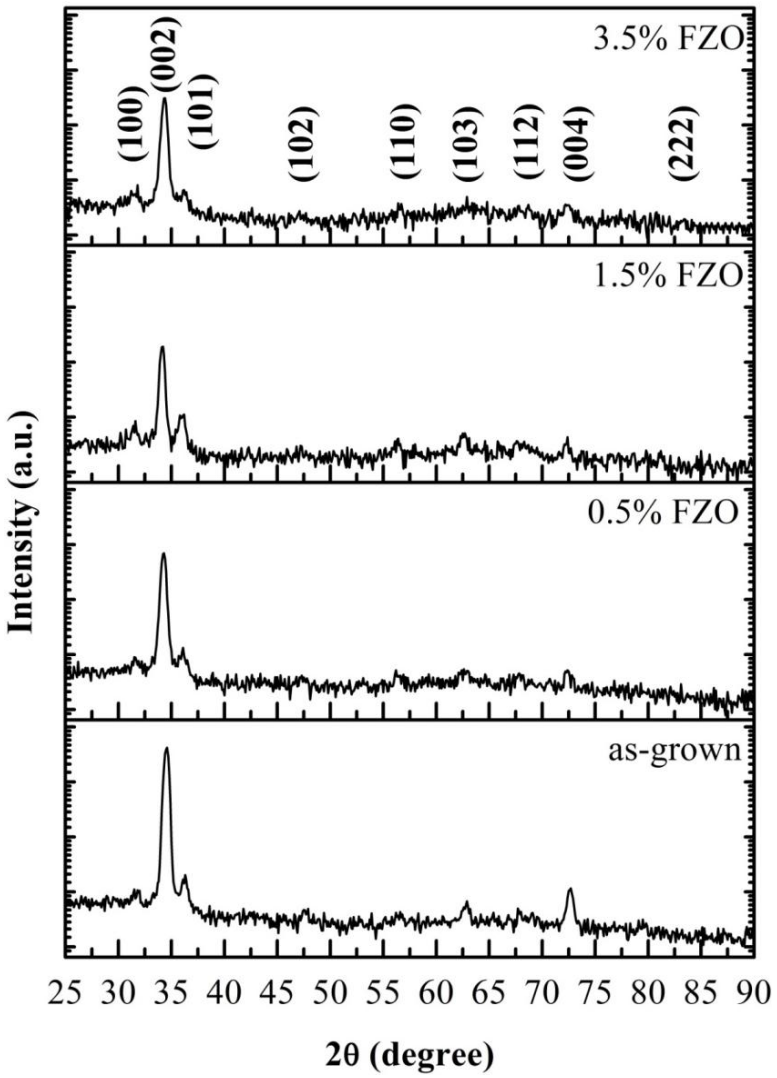

Figure 1. XRD patterns of ZnO thin films with different fluorine contents.

ZnF_2. Probably, this could be the reason for reduced XRD peak intensity. If excess fluorine atoms do not occupy the proper lattice positions, instead of occupying interstitial sites (like ZnF_2) (Tsai et al., 2010), the crystallinity of ZnO having highly F concentrations may be deteriotated. The calculated interplaner distance *d* values from XRD studies were presented in Table 1 and these values were compared with the standard ones from JPCDS card no: 36 to 1451. The matching of the calculated and standard *d* values confirms that the deposited films are of ZnO with a hexagonal wurtzite structure. Also, the lattice constants *a* and *c* of the wurtzite structure of ZnO can be calculated using the relations as follow (Sakthivelu et al., 2011):

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

Where *d* and (*hkl*) is the interplaner distance and Miller indices, respectively. The standard and calculated lattice constants were given in Table 2. The calculated *a* and *c* values agree with JPCDS card no: 36-1451. As seen from Table 2, F doping did not affect much lattice constans of ZnO. The crystallite size of the ZnO films doped at different F doping concentrations was calculated by using Scherrer's formula (Bowen et al., 2011):

$$D = \frac{0{,}9\lambda}{\beta cos\theta}$$

Where *D* is the crystallite size, wavelength of the X-ray used is λ =1.5418 Å, β is the broadening of diffraction line measured at the half of its maximum intensity in radians (belong to (002) peak) and θ is the angle of diffraction. The number of crystallites per unit area (N) of the films was determined using the following relation

Table 1. Standard and observed interplanar distances'*d*' values of the films.

(hkl)	Standard d (Å)	Observed d (Å)			
		Undoped ZnO	0.5% FZO	1.5% FZO	3.5% FZO
100	2.814	2.837	2.8148	2.8408	2.8316
002	2.603	2.592	2.6060	2.6128	2.6211
101	2.475	2.473	2.4833	2.4856	2.4816
102	1.911	1.911	1.9290	1.9265	1.9265
110	1.624	1.623	1.6243	1.6365	1.6295
103	1.477	1.476	1.4783	1.4769	1.4809
112	1.378	1.384	1.3832	1.3821	1.3868
004	1.301	1.299	1.3039	1.3045	1.3049
ZnF_2 or NH_4ZnF_3	-	-	-	-	1.1407

Table 2. The structural parameters of undoped and F doped ZnO thin films.

Sample (% mole F doped)	Lattice constants (Å)		D (nm)	N (x10^{16}m^{-2})
	a	c		
0.0	3.2498	5.1830	16	10
0.5	3.2503	5.2120	15	12
1.5	3.2629	5.2256	16	10
3.5	3.2697	5.2422	18	7

JPCDS card no: 36-1451 (a = 3,250 Å and c = 5,207Å).

(Ravichandran et al., 2010); $N = t / D^3$ Where, *t* is the thickness of the film and it was about measured to be 417 nm for the samples. Table 2 gives the crystallite size and the number of crystallites per unit area along prominent diffraction planes for films. The grain size firstly shows a decreasing tendency at 0.5% mole F doped, then again shows increasing beyond of 0.5% mole F dopant content. Whereas, the number of crystallites per unit area was shown a tendency opposite to relation of the grain size with F doping content as an expected result.

Figure 2 shows the scanning electron micrograph (SEM) micrographs of the films doped at different fluorine content. All the FZO films show good homogeneity and have uniform grains and smooth surface; these properties imply the well crystallinity, which is effective on the characteristics of the device (Cao et al., 2011). It is clear from these micrographs that the surface morphology of FZO films were modified with doping. A clear change in the grain size due to the effect of the doping can be observed. It can be seen that the grain size gradually increased with F doping range from 0.5 to 3.5% mole. The images show that the films have columnar grained structure perpendicular to the substrate surface. This result confirms the XRD patterns indicating c-axis orientation growth. Similar to our study, it has been pointed out by many groups that sol-gel derived thin films exhibited most likely particle-like microstructures on the film surface (Lee et al., 2003; Zhou et al., 2007; Chen et al., 2008).

Optical transmittance spectra of FZO samples and undoped ZnO were recorded in the wavelength range 350 to 900 and 365 to 425 nm and are given in Figure 3. The transmittance spectra show interference fringes. The appearance of interference fringes indicates smooth reflecting surface of the film and minimum scattering loss at the surface, which indirectly proved the homogeneous film deposition. Undoped film exibits 65% transmittance, when fluorine incorporates in ZnO, the transmittance of the film sharply increase to 90 to 95% in transmittance at about 400 nm. The transmittance in the short wavelengths shows a proportional increase with increasing fluorine content. The increase in transmittance spectra at the edge of UV region can be due to increase in oxygen sites occupied by fluorine which is related to increase in carrier concentration, commonly known as the Burstein–Moss effect (Pawar et al., 2008). A peak observed at 3.2 eV (about 385 nm) could be explained by the exciton transition. The exciton effect has been observed in ZnO at room temperature by Yakuphanoglu et al. (2007). The optical band gap can be calculated from the following relationship (Tauc, 1974):

$$(\alpha h\nu) = A(h\nu - E_g)^m$$

Where α is the optical absorption coefficient in cm^{-1}, *A* is the absorbance, *m* is a constant which determines type of the optical transition (m = 1/2 for allowed direct transitions and m = 2 for allowed indirect transitions). Optical band

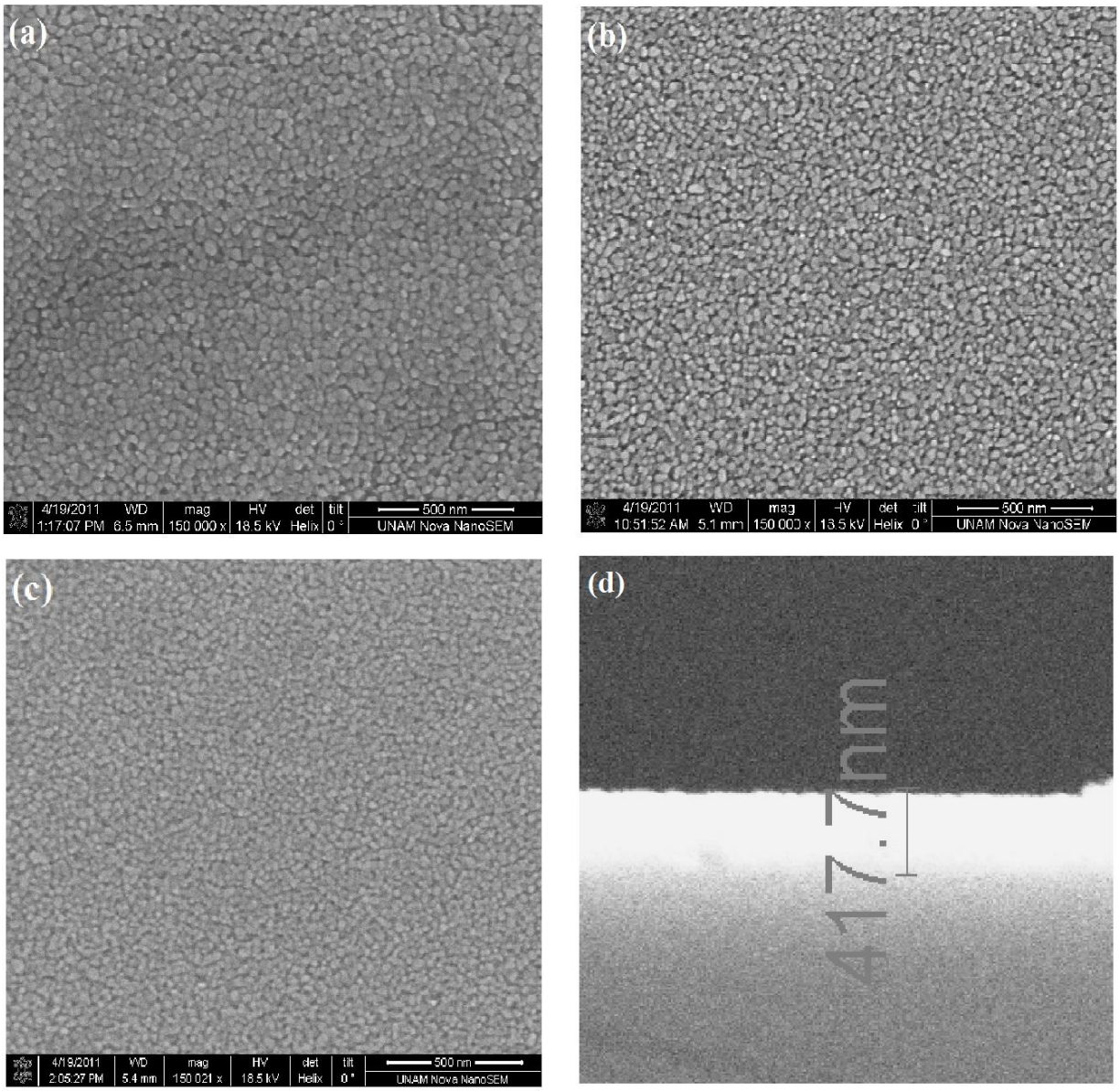

Figure 2. SEM micrograph of ZnO films with different fluorine concentrations: (a) $F_{0.5}ZO$; (b) $F_{1.5}ZO$; (c) $F_{3.5}ZO$; (d) cross sectional SEM image for avarege film thickness (0.5% mole).

gap values were determined from the plot of $(\alpha h\nu)^2$ versus photon energy graph. This curve was shown in Figure 4, depending on fluorine content. The band gap of 3.270 eV for undoped was increased to 3.291 eV for the sample having 0.5% mole doping and 3.293eV for the one having 1.5% mole doping. Again it decreased to 3,287 eV for 3.5% mole doping, respectively. Although the band gap of ZnO is about 3.4 eV, it is about 7 to 8 eV for ZnF_2 (Tsai et al., 2009). It can be easily seen that the band gap has been affected by the substitution or interstitial of flourine with oxygen and this process has reduced the carrier concentration due to the valence number of fluorine is one less compared to oxygen.

Conclusion

In this work, transparent and conductive fluorine-doped ZnO (FZO) thin films have been deposited by sol-gel spin-coating method. The obtained data show that the crystal morphology and structure of ZnO is highly affected by F doping. The intensity of (002) peak of undoped sample decreases with increasing F doping concentration as a result of deterioration the film crystallinity. The peak which is belonging to ZnF_2 was observed very weakly because of high volatility of fluorine. From SEM micrograph, it was observed that surfaces of doped F films exhibited uniform particle-like

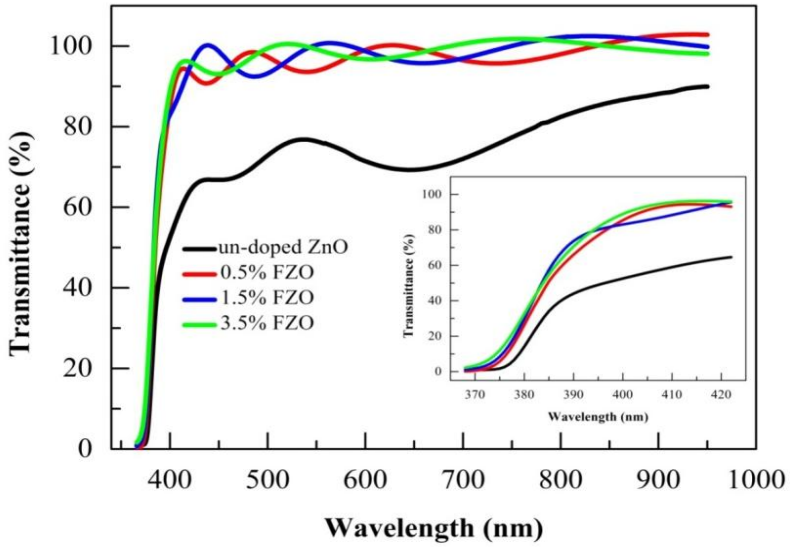

Figure 3. Optical transmittance spectra of un-doped and various F-doped ZnO films and inset figure shows the transmittance spectra at short wavelengths.

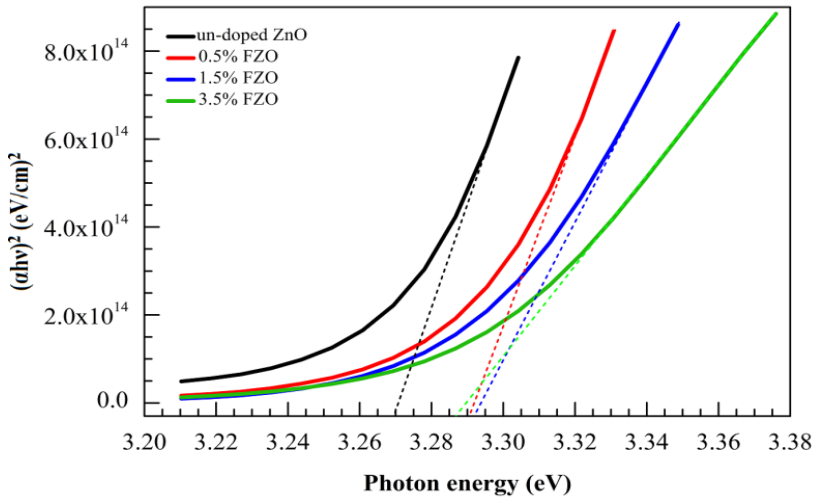

Figure 4. Plot of $(\alpha hv)^2$ versus photon energy for F-doped ZnO thin films.

and granular morphologies and were affected by the flourine incorporation. Increased doping concentrations from 0.5 to 3.5% mole have increased the grain sizes in FZO films. The grain size of the undoped ZnO and 0.5, 1.5 and 3.5% mole F doped ZnO was calculated 16, 15, 16 and 18 nm, respectively. The interplanar distance between standard and calculated values for the films did not show differences and this could be indicated that ZnO films having a hexagonal wurtzite structure. FZO films exhibited better transparency than undoped ZnO film with highly transparency in the visible region. In conclusion, doping of fluorine into ZnO films with specific metallic dopant content can be a promising material TCO as the electrodes of thin film solar cell application because of their good transparent properties integrated with their beneficial effect of improving optical and structure properties.

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