



# Properties of fluorine-doped ZnO deposited onto glass by spray pyrolysis

A. Sanchez-Juarez<sup>a,\*</sup>, A. Tiburcio-Silver<sup>b</sup>, A. Ortiz<sup>c</sup>

<sup>a</sup>Centro de Investigación en Energía – UNAM P.O. Box 34, 62580 Temixco, Morelos, Mexico

<sup>b</sup>Div. de Estudios de Posgrado, Instituto Tecnológico de Toluca, SEP, Mexico

<sup>c</sup>Materials Research Institute (IIM)-UNAM, D.F., Mexico

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## Abstract

Fluorine-doped ZnO (FZO) thin films were deposited onto glass by the spray pyrolysis process, using zinc acetate and  $\text{NH}_4\text{F}$  as precursors. The role of F/Zn atomic ratio, in the starting solution, and the substrate temperature were investigated and the optimum deposition conditions have been outlined. The X-ray diffraction analyses of the films show that there is incorporation of F atoms in the film. The FZO films are of polycrystalline nature with a preferential growth along (0 0 2) plane parallel to the surface of the substrate for temperatures higher than 400°C. It is observed that fluorine incorporation in the films affects the grain size, which decreases as the F/Zn atomic ratio increases, for the same substrate temperature. The films are uniform and exhibit an optical transmittance above 85% in the visible region. A critical substrate temperature (425°C) was observed at which the films show an n-type electrical dark conductivity as high as  $9 (\Omega \text{ cm})^{-1}$  when using a solution flow rate of 16 ml/min and a gas flow rate of 10 l/min. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluorine-doped ZnO; Thin films; Spray pyrolysis

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## 1. Introduction

In the last few years, interest in transparent conducting films of non-stoichiometric and doped metallic oxides (such as  $\text{SnO}_2$ ,  $\text{CdO}$ ,  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2 : \text{In}$ ,  $\text{SnO}_2 : \text{F}$ ,  $\text{ZnO} : \text{In}$ ,  $\text{ZnO} : \text{F}$ ,  $\text{Cd}_2\text{SnO}_4$ ) has increased markedly, because of their high electrical conductivity and optical transmittance in the visible region of the solar spectrum,

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\* Corresponding author.

together with their high reflectance in the IR. These materials have a wide variety of applications in modern optoelectronic and photovoltaic devices [1–3]. Among these materials, zinc oxide (ZnO) is a technologically important material. It is relatively less expensive than others and possesses a very sharp UV cut-off; these characteristics are, therefore, advantageous in many cases. ZnO has been used as an n-type conducting window in thin film solar cells based on cadmium telluride [4] or indium diselenide [5]. Due to the lack of chemical interaction between the plasma-deposited a : Si : H and ZnO, this material has been used as a window layer in amorphous silicon solar cells [6–8]. There are many processes by which these layers can be prepared on glass substrates, but the well known spray pyrolysis process is one relatively easy and cheap method, suitable for deposition of ZnO thin films. This technique is also compatible with mass production systems. Stoichiometric ZnO has a high electrical resistivity with an energy band gap of about 3.3 eV and a low reflectivity in the IR region [9]. Non-stoichiometric ZnO, in general, is an n-type material, with a high electrical conductivity due to lack of oxidation or excess zinc, but it is not stable at high temperatures. Heat treatment, at atmospheric pressure, of non-stoichiometric films at 400°C increases the sheet resistance by a factor of about  $10^3$  [10]. The electrical conductivity of sprayed ZnO films can be further improved by doping it with indium or aluminum at cation sites [11]. Halogens like Cl [12,13] and F [14] can also act as dopants in ZnO thin films by anion substitution, replacing the oxygen. We can find in the literature that the physical properties of sprayed ZnO thin films are strongly affected by doping of cation sites, but only a few works has been reported on ZnO thin films doped at anion sites. Still, a systematic study of the effect of doping at anions sites on the physical properties and correlation between them is lacking.

In this work, we present results of investigation on the changes in properties of fluorine-doped ZnO films deposited by the spray-pyrolysis process. The observed changes in the structural, electrical, and chemical composition are shown as functions of the deposition parameters

## 2. Experimental

In the spray pyrolysis technique there are many deposition variables (the parameters of the process), such as substrate temperature, gas and solution flow rates, composition and concentration of the precursor in the starting solution, deposition time, the substrate-nozzle distance, etc. Some of these parameters are mutually dependent on each other. However, to study the effects of any one of these, the remaining others must be kept constant. Taking into account the work carried out by Aranovich et al. [13] and our previous reported work [15,16], the molar concentration of the source materials in the starting solution for a given solvent, the substrate-nozzle distance, and the gas and solution flow rates were maintained constant.

### 2.1. Sample preparation

The ZnO : F thin films (FZO) were deposited by the spray pyrolysis technique onto Pyrex glass slices of  $1.5 \times 2.5$  cm, chemically and ultrasonically cleaned. The film

deposition is done when a jet of fine drops of the starting solution is driven by the carrier gas towards the heated surface of the substrate where the pyrolytic reaction occurs. The system used for the deposition process is similar to that reported in Ref. [13]. Air at a pressure of 40 psi was used as the carrier gas. The gas flow rate ( $F_{go}$ ) and the solution flow rate ( $F_{so}$ ) were 10 and 16 ml/min, respectively, in all cases. The substrate-nozzle distance was of 30 cm. In this work, we used a 0.05 M zinc acetate dihydrate dissolved in a mixture of three parts of methanol and one part of deionized water. The substrate temperature ( $T_s$ ) was varied from 300°C to 500°C in 25°C steps, and it was electronically controlled and measured with a chromel–alumel thermocouple located under the substrates. An uncertainty in  $T_s$  of about  $\pm 5^\circ\text{C}$  was unavoidable. Fluorine doping was achieved by adding ammonium fluoride to the starting solution and the doping level was controlled by means of the F/Zn atomic ratio which was varied from 0.0 to 1.0 in 0.1 steps.

In order to understand the role of  $T_s$  and F/Zn on the physical properties of the FZO thin films, we used a deposition time of 10 min in order to know the deposition rate, and then, to fix the thickness of the films at  $t \approx 0.2 \mu\text{m}$  for characterization purposes.

## 2.2. Film characterization

The thickness of the films was measured by means of a profilometer Alpha Step 100 from Tencor Instruments. The required step was made during the deposition of the film. The measured thickness was confirmed by an optical technique. The structural properties were studied by X-ray diffraction measurements (Siemens D-500) using the  $\text{CuK}_\alpha$  radiation with  $\lambda = 1.5405 \text{ \AA}$ . The preferential orientation of the crystalline structure was studied using the Foster's procedure [17] and the average dimension of the crystallites was determined by Scherrer's method from the broadening of the diffraction peaks taking into account the instrumental broadening. The optical reflectance  $R$  and transmittance  $T$  in the UV-VIS-NIR region (300 to 2500 nm) were measured with a double-beam spectrophotometer Shimadzu 3101PC. All optical measurements were performed using air as the reference. The average optical transmittance in the visible region for a naked clean substrate was 91% using again air as the reference. The amount of irradiance passing through the FZO thin films, useful for solar cell applications, was measured with an Eppley Radiometer PSP. For this purpose, a solar simulator Oriel Mod 81174 was used. The lateral electrical conductivity measurements, for the films at room temperature, were automatically carried out by the four-point probe method. Electrical contacts to the films were made with four indium strips deposited by vacuum thermal evaporation.

## 3. Results and discussions

### 3.1. Growth characteristics

Since our main goals were to know the effects of fluorine incorporation and the substrate temperature on the physical properties of spray-pyrolysis-deposited ZnO

thin film, it was necessary to produce undoped films at different  $T_s$ , without fluorine in the starting solution. To analyze the fluorine doping effect, doped films were deposited at the same deposition conditions. Fig. 1 shows the growth rate as a function of the substrate temperature for different F/Zn ratios. It is evident from the figure that the growth rate decreases as the substrate temperature increases, with a trend for a constant value for higher  $T_s$ . This behavior has been observed by Aranovich et al. [13] and Eberspacher et al. [18] for undoped sprayed ZnO thin films prepared from a zinc acetate solution and deposited onto glass and InP substrates, respectively. They concluded that the kinetics of growth is governed by the behavior of droplets as they impinge on the heated substrate, i.e. the lateral mobility of the droplets and the coalescence and sintering kinetics of the overlapping disk crystallites determine the growth kinetics and microstructural features of the sprayed ZnO thin films. Fig. 1 shows that fluorine-doped ZnO films have higher growth rate than that observed in undoped ZnO films.

Optical micrographs and SEM micrographs [16] of our films show that for  $T_s$  lower than  $450^\circ\text{C}$ , circular features with an average diameter of about  $10\ \mu\text{m}$  are located on the surface and underneath the surface, which imply that wetting occurs. Then the reaction proceeds slowly and some quantity of the precursor and doping compound must remain in the film at substantial proportions; consequently, high growth rates are expected. As the substrate temperature increases, wetting decreases, and splitting, bouncing and the lateral mobility of the droplets increases. Laterally moving droplets, in which the reactions proceeds more slowly, could be swept away by the air stream and lower growth rates are expected. At substrate temperature higher than  $450^\circ\text{C}$ , the solvent is evaporated before the droplets reach the substrate

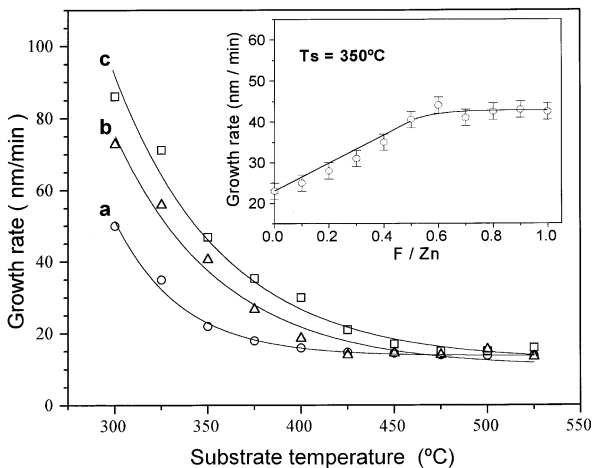


Fig. 1. Growth rate of sprayed ZnO:F films as a function of substrate temperature for different F/Zn ratios. (a) F/Zn = 0.0; (b) F/Zn = 0.7; (c) F/Zn = 0.6. The inset shows the variation of the growth rate vs. F/Zn ratio for  $T_s = 350^\circ\text{C}$ .

and the process is controlled by a CVD reaction. Then the kinetics of growth must be controlled by diffusion resulting in a trend to a constant value for the growth rate.

On the other hand, Fig. 1 indicates that fluorine incorporation on the ZnO thin films enhance the growth rate. It is well known that in a process like spray pyrolysis the growth mechanism is determined by nucleation type and nucleation rate [20]. The creation of the nucleation centers is influenced by the presence of the adsorbed impurities [21] and then we can expect that fluorine incorporation increases the number of nucleation centers on ZnO thin films. To study the effect of F/Zn ratio on the growth rate of FZO thin films, we chose  $T_s = 350^\circ\text{C}$ , due to the fact that for this temperature the pyrosynthesis of zinc acetate shows that the final product is only solid ZnO [19]. The inset in Fig. 1 shows the dependence of growth rate on F/Zn for  $T_s = 350^\circ\text{C}$ . We can see that the growth rate increases linearly up to  $\text{F/Zn} \approx 0.7$  followed by a constant value at approximately 42.5 nm/min. This kind of growth is explained if it is considered that more nucleation centers are created as F/Zn ratio in the solution increases. Further growth is governed by surface mobility of the adatoms [21] and the behavior of the growth rate with respect to F/Zn atomic ratio seems to suggest that this mobility is first increased and then saturates as the fluorine content in the solution increases.

### 3.2. Structural properties

In previous works [15,16], we found by X-ray diffraction measurements that undoped ZnO thin films prepared by spray pyrolysis at different substrate temperatures are of polycrystalline in nature with a hexagonal wurtzite structure. We calculated the degree of preferred orientation in these films using the Foster's procedure [17]. We found that the preferred growth in undoped ZnO thin films is dependent on the substrate temperature. For  $T_s = 300^\circ\text{C}$ , the films show a preferred growth along the  $[1\ 0\ 0]$  direction, and when  $T_s$  increases, an enhancement in the preferred orientation along  $[0\ 0\ 2]$  direction is observed. This preferred orientation has been observed for  $T_s \geq 400^\circ\text{C}$ . Others peaks  $(1\ 0\ 2)$  and  $(1\ 0\ 3)$  are also observed, but their intensity is very small compared to that of the  $(0\ 0\ 2)$  peak. For higher substrate temperatures a grain growth strongly oriented along the  $[0\ 0\ 2]$  direction is observed indicating a preferential orientation of the crystallites with the  $c$ -axis perpendicular to the substrate surface (see Fig. 2a). These results are in concordance with the properties of ZnO thin films prepared by the same process [13,22].

Taking into account the fact that fluorine incorporation on sprayed ZnO thin films, prepared at  $T_s = 300^\circ\text{C}$ , decreases the crystallinity of the deposited films [15], and for undoped ZnO prepared at  $T_s \geq 425^\circ\text{C}$  the films have a preferential growth along the  $[0\ 0\ 2]$  direction, we choose a substrate temperature of  $425^\circ\text{C}$  in order to study the effect of F/Zn ratio on the preferential growth. Fig. 2b and Fig. 2c show X-ray diffractograms of fluorine-doped ZnO films prepared at  $T_s = 425^\circ\text{C}$  and  $T_s = 375^\circ\text{C}$ , respectively. We can see that the doped ZnO films prepared at  $T_s = 375^\circ\text{C}$  are formed as an unoriented polycrystalline material, while at  $T_s = 425^\circ\text{C}$ , an increase in F/Zn

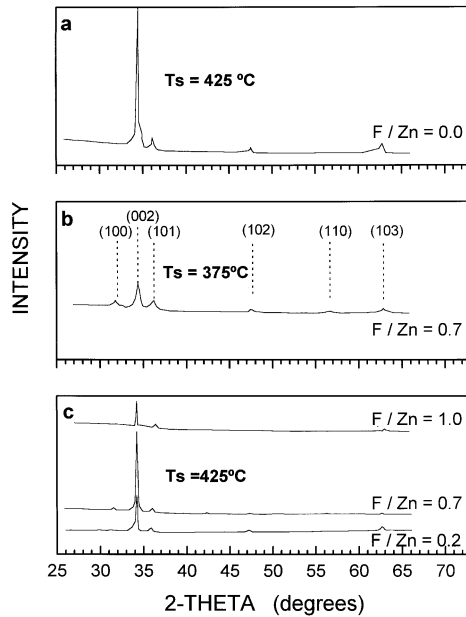


Fig. 2. X-ray diffractograms of (a) undoped ZnO prepared at  $T_s = 450^\circ\text{C}$ ; (b) doped ZnO with a F/Zn = 0.7 ratio and prepared at  $T_s = 375^\circ\text{C}$ ; (c) doped ZnO with different F/Zn ratios prepared at  $T_s = 425^\circ\text{C}$ .

ratio does not affect the preferential growth of the films. It is clear from these diffractograms that there is an effect in the grain size due to fluorine incorporation in the film.

The grain size of the films was estimated from the full-width at half-maximum of the peak with highest intensity in all cases [23]. In the present  $T_s$  range used, the grain size increases as  $T_s$  increases showing approximately a linear behavior. The values found for the grain size are in the range 18–42 nm which agrees with the values reported in the literature [18]. From Fig. 3 it can be seen that as long as the F/Zn increases the grain size of the films decreases. This effect can be explained if it is considered that (a) fluorine atoms do not substitute oxygen atoms, instead they occupy interstitial sites resulting in a large number of dislocations and (b) probable formation of a compound which is growing along with ZnO:F. It has been found that the corrosion of a Zn–Al–Cu alloy by fluorine gas takes place at a temperature of 523 K and an unstable compound with ZnF<sub>2</sub> stoichiometry appears [24]. Then it is possible to get ZnF<sub>2</sub> in fluorine-doped sprayed ZnO thin films. If it is considered that the bonding energy of F–Zn (88 kcal/mol) is larger than that of the O–Zn bond (67.9 kcal/mol) [25], then the formation of F–Zn molecules is more probable than the formation of O–Zn molecules. Hence, if the NH<sub>4</sub>F concentration increases in the starting solution, the F–Zn increases and then a growth competition between ZnO and ZnF<sub>2</sub> takes place.

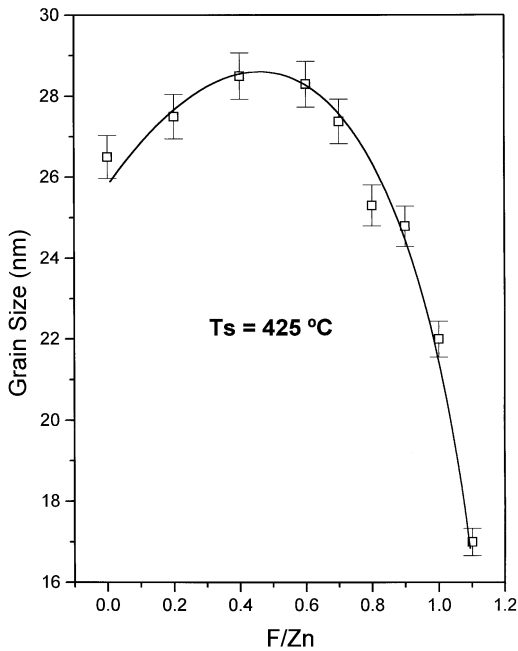


Fig. 3. Dependence of grain size on the F/Zn ratio for sprayed ZnO thin films prepared at  $T_s = 425^\circ\text{C}$ .

### 3.3. Optical properties

In order to know the amount of irradiance passing through the FZO films, useful for a solar cell application, we define the mean transparency of the films ( $T_p$ ) as transmitted/incident irradiance ratio with reference to the glass substrate. Fig. 4 shows the mean transparency as a function of the F/Zn ratio for three values of  $T_s$ . These curves show that an increase in the substrate temperature produces an increase in the  $T_p$  values associated with an efficient pyrolytic decomposition of the sprayed solution, while lower substrate temperatures produce whitish appearance of films with lower  $T_p$  values. It was also found that a lower substrate temperature produces unoriented polycrystalline microstructure, while a high substrate temperature produces films with high optical transmittance showing better crystallinity [15,16]. Fig. 4 depicts that F/Zn ratio does not affect the mean transparency of the films up to the higher doping levels, in which  $T_p$  goes down. For these high doping levels at lower  $T_s$  the observed behavior could be attributed to the textured surface of the film and powdery nature of the deposited material. At high substrate temperatures and high doping levels, the films have a whitish appearance, and the addition of more  $\text{NH}_4\text{F}$  in the starting solution inhibit the ZnO crystal growth as it was suggested by X-ray diffraction patterns. On the other hand, these conditions favor the formation of the new compound ( $\text{ZnF}_2$ ) as has been suggested.

Fig. 5 shows the transmittance and specular reflectance of undoped and fluorine-doped (F/Zn = 0.4, 0.7) ZnO thin films deposited at  $T_s = 425^\circ\text{C}$ . The transmittance is

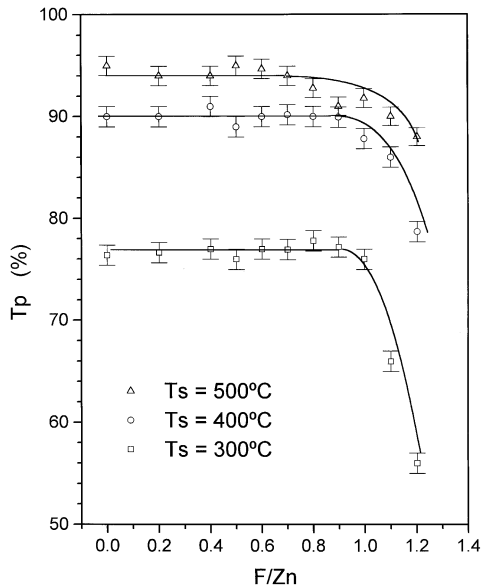


Fig. 4. Transparency behavior of doped ZnO thin films prepared at different substrate temperatures.

about 80–90% for the wavelength range 450–2500 nm. It can be seen that in the visible region, the transmittance is limited only by the surface reflectance of about 15%. For wavelengths in the absorption edge region it is observed that it is shifted towards lower wavelengths associated with an increase of the F/Zn ratio. This effect has been already observed and discussed by other authors [26] and, at present, we are studying more closely this wavelength region and our results will be reported in the near future [27].

### 3.4. Electrical properties

The electrical dark conductivity ( $\sigma$ ) of FZO thin films was measured using the four-point probe technique assuming homogeneous conduction throughout the depth of the film. The dark conductivity of doped and undoped zinc oxide thin films are shown in Fig. 6 as a function of substrate temperature for different F/Zn ratios. It is seen that, in general, fluorine incorporation in the film improves the dark conductivity. For the sample with F/Zn = 0.7, the dark conductivity ( $\sigma$ ) increases up to three orders of magnitude. On the other hand, a region of maximum conductivity centered around  $T_s = 425^\circ\text{C}$  is found. All the films exhibit n-type conductivity which was confirmed by the hot-point probe method.

Taking into account the polycrystalline nature of the FZO films it is considered, in order to explain the conductivity behavior in Fig. 6, that the reaction residues or other compounds produced in the process must be located at grain boundaries or surfaces but not inside the crystallites.



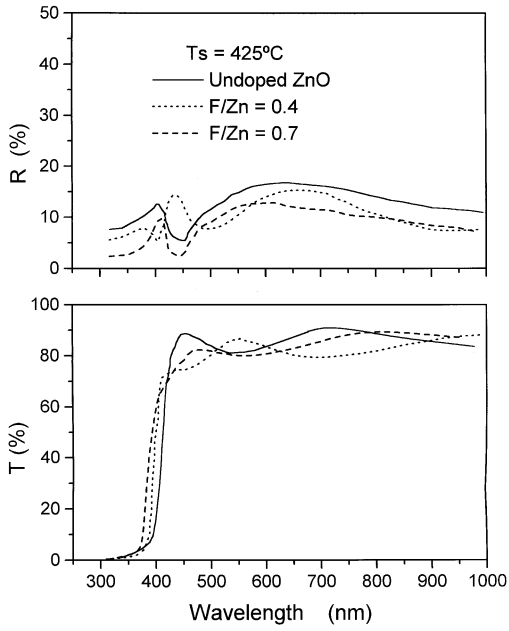


Fig. 5. Specular reflectance  $R$  and transmittance  $T$  spectra of an undoped and fluorine doped ZnO films prepared at  $T_s = 425^\circ\text{C}$ .

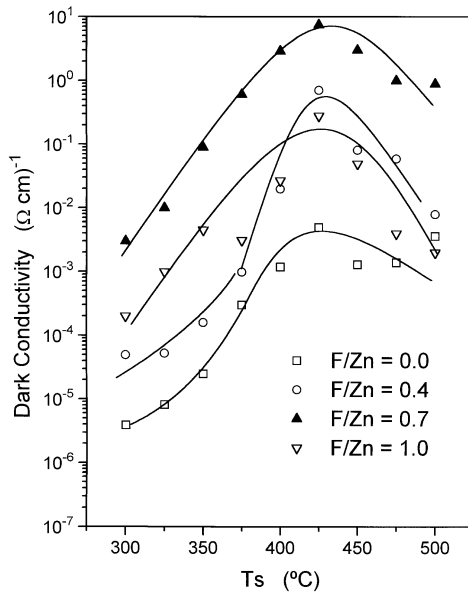


Fig. 6. Plots of dark conductivity vs. substrate temperature for sprayed doped and undoped ZnO films.

*Undoped ZnO films:* It can be observed in Fig. 6 that at lower temperatures, the  $\sigma$  value is low and the ZnO films show a quasi-intrinsic behavior [15,16]. An increase in the substrate temperature leads to higher values for  $\sigma$ . It is well known that the n-type conductivity in undoped non-stoichiometric ZnO is due to the oxygen vacancy and interstitial zinc atoms, both act as donors [28], giving rise to a high carrier concentration as  $T_s$  increases. On the other hand, films deposited at high  $T_s$  show a better lattice order and larger grain size. The increase in the  $\sigma$  values up to  $T_s = 425^\circ\text{C}$  could be associated with a combination of the above-mentioned effects. However, we cannot explain the decreasing behavior observed in the electrical dark conductivity for samples prepared at  $T_s > 425^\circ\text{C}$ .

*Fluorine-doped ZnO films:* Fluorine was found to be an n-type dopant for ZnO, which increases the electrical dark conductivity probably due to an increase in the free-electron concentration. Films prepared at  $425^\circ\text{C}$  with F/Zn ratio of 0.7 gives the highest conductivity.

Fig. 6 suggests that the deposition temperature can strongly influence both the reactivity of the dopant compound and the movement of dopant atoms to electrically active positions. Hu and Gordon [14] found the same behavior for FZO thin film prepared by CVD. They found that the doping efficiency increases as the temperature increases. To explain the behavior shown in Fig. 6 it is necessary to know the fluorine concentration in the film and to find out the doping efficiency of the compound. On the other hand, we can see in Fig. 6 that as more fluorine is added to the starting solution, the film conductivity first increases and then decreases. As the highest conductivity is found for the films with the highest grain size, the decreasing  $\sigma$  for F/Zn = 1.0 could be due to the reduction in the grain size, observed in this sample, which reduces the majority carrier mobility because the scattering process is increased. However, if we consider that an increase in F/Zn ratio in the starting solution produces an increase in the fluorine incorporation in the film, then the high fluorine concentrations will also increase the scattering process and therefore the majority carrier mobility is decreased.

#### 4. Conclusions

Fluorine-doped zinc oxide films have been prepared by the spray pyrolysis technique. The fluorine incorporation in the sprayed ZnO thin film affects the structural and optoelectronic properties. For films prepared at low substrate temperature, the fluorine incorporation enhances the growth rate and affects the structural properties. For this  $T_s$  range, the films show an unoriented crystalline structure. At high substrate temperatures, the crystalline structure of the films are oriented with the c-axis perpendicular to the surface of the substrate. At  $T_s \geq 450^\circ\text{C}$ , the growth rate does not show significant changes and has a trend similar to that observed for undoped ZnO prepared under the same conditions. The transparency of FZO films is independent of the doping levels for F/Zn ratio less than 0.9. The fluorine-doped ZnO films deposited under optimum conditions, exhibit attractive transparent conducting properties suggesting a photovoltaic application. Typically, a ZnO : F film prepared at  $T_s = 425^\circ\text{C}$

using F/Zn ratio of 0.7 with a thickness of 2000 Å has a transparency of about 90% and an electrical dark conductivity of about  $9 (\Omega \text{ cm})^{-1}$ .

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