

Structural, Optical and Electrical Properties of ZnO:Fe Thin Films Grown by Spray Pyrolysis

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Received date: May 25, 2014; revised date: December 20, 2014; accepted date: December 21, 2014

Abstract

We present the influence of Fe-doping (2%, 3% and 4%) on ZnO thin films. For this purpose, structural, electrical and optical proprieties have been investigated by X-ray diffraction, 4-points technique and UV-Visible spectrophotometry. The ZnO:Fe thin films have been deposited by pneumatic spray pyrolysis on glass substrates at different temperatures (350, 400 and 450°C) and fixed molarity (0.1mol/l). The precursor solution is a mixture of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) dissolved in bi-distilled water. The X-ray diffraction (XRD) analyzes show that all the prepared thin films have a polycrystalline structure dominated by (100), (002) and (101) textured orientations. A resistivity of $2.9 \cdot 10^2 \Omega \cdot cm$ was found for films deposited at 450°C with an iron rate of 3%. The average transmittance was found to be in the range of 45-70% for the different doping rates. The optical band gap energy of the films was found near 3.3 eV.

key words: Thin films, Spray pyrolysis, ZnO:Fe, Resistivity, Band gap energy.

1. Introduction

Zinc oxide (ZnO), a II-VI semiconducting material with a wide direct band gap of 3.3 eV [1], has an advantage of independently controlled charge by changing the doping rate by a transition-metal element (Mn, Co, Fe, etc.) [2-4]. The transition metal-doping in ZnO is very attracting [5] because it leads to new interesting properties [6,7] and is a good candidate method to improve optical properties. In order to use ZnO thin films in an optoelectronic device, the performances of the device have to be adjusted by controlling the optical, structural and electronic properties of the films. Bae et al. [8] reported that ZnO thin films showed different emission bands depending on the doping material.

ZnO:Fe semiconductors have a number of attractive applications, such as: gas sensor devices [9], transparent electrodes [10], piezoelectric devices [11], etc. Several techniques have been used to produce many distinct zinc oxide films: chemical vapor deposition [12], radio frequency magnetron sputtering [13], Sol-Gel [14], spray pyrolysis, etc. [15-18]. In this work, we have investigated the properties of ZnO-doped films deposited by spray pyrolysis. For this purpose, the optical, structural and electrical properties of Fe-doped ZnO were studied when

varying Fe content and substrate temperature. In order to determine the doping effect of the transition metal (²⁷Fe) in ZnO on these properties, we carried out UV-Visible spectro-photometry, DRX analysis and 4-points measurements, respectively.

2. Experimental

A spray pyrolytic technique was used to obtain Fe doped zinc oxide thin films. The experimental set up was previously described [20, 21]. The films were prepared by a solution with fixed concentration (0.1 mol/l) of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) dissolved in doubly distilled water onto glass substrates. The substrate temperature was varied between 350 and 450°C and measured via a Chromel-Alumel thermocouple. X-ray diffraction was used to determine the crystallographic structure. The size of crystallites were estimated using the Scherrer's formula [22]:

$$D = \frac{0.9 \lambda_X}{\beta \cos \theta} \quad (1)$$

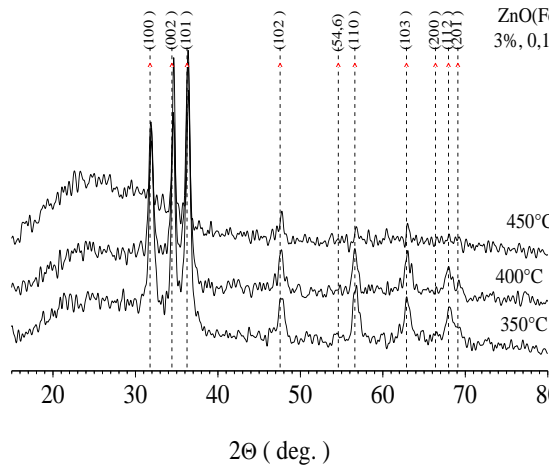


Fig.1. X-ray diffraction patterns of doped ZnO by 3% of iron thin films deposited by spray pyrolysis using different temperatures at 0.1M.

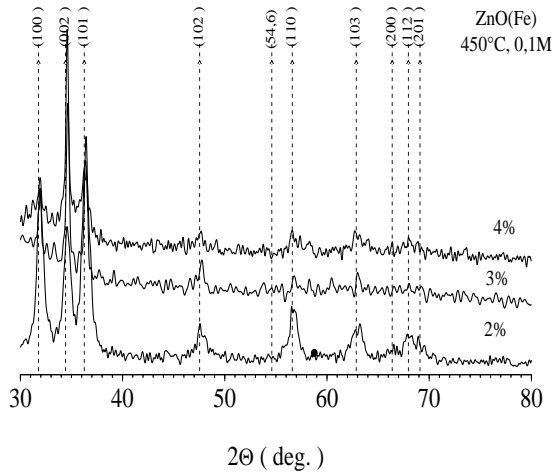


Fig.2. X-ray diffraction patterns of ZnO:Fe thin films deposited by spray pyrolysis using different doping rates at fixed molarity (0.1M) and temperature (450°C).

where λ_x , θ and β are the X-ray wavelength (1.54056 Å), Bragg diffraction angle of XRD peak in degrees, and the full width at half maximum (in radian) of [002], [101], [100] orientations, respectively.

The optical transmission spectra $T(\lambda)$ of the films were obtained using the Shimadzu-3101PC UV-Vis-NIR spectrophotometer. From these spectra the values of the optical energy gap were deduced using formula (2) for direct band gap semiconductors [23]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where A is a constant. E_g is obtained from $(\alpha h\nu)^2$ vs. $h\nu$ plot when $(\alpha h\nu)^2=0$. The absorption coefficient α

is deduced from $T(\lambda)$ through the Beer-Lambert law [24]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad (3)$$

where d is the film thickness. Another important parameter that characterizes the disorder in the material is Urbach energy parameter (E_{Urb}) determined from Urbach law [25,26]:

$$\ln \alpha = \ln \alpha_0 + \frac{h\nu}{E_{\text{Urb}}} \quad (4)$$

The electrical properties of the films were determined using the I-V characteristics measured by the 4-points technique.

3. Results and Discussion

a. Structural Characterization

Typical XRD patterns of ZnO:Fe thin films with various rates of iron doping (2%, 3% and 4%) are presented in figures 1 and 2. In all cases, the observed diffraction peaks are indexed to standard hexagonal wurtzite ZnO structure. No secondary phases or impurity peaks can be identified which demonstrates that the dopant is well integrated into the lattice sites during the synthesis process. A small shift of the peaks to higher angles with the increase of Fe doping compared to those of pure ZnO was observed. The minor peak shift is usually assigned to the successful incorporation of dopant irons in the host matrix [27]. The lattice constants of Fe (3%) doped ZnO ($a=3.2405$ Å, $c=5.2112$ Å) were found to be slightly larger than those of pure ZnO ($a=3.2491$ Å, $c=5.2062$ Å). This observation is similar to the case in transition metal (Mn, Cu and Ni) doped ZnO studied by Ekambaram et al. [28].

The variations of estimated grain size D with temperature and doping rate are represented on figure 3. The size of the grains increases from 100 to 335 Å when the percentage of doping varies from 2 to 4% and the temperature change between 350 to 450°C at fixed concentration. This evolution is normal because the increase in the percentage of doping or treatment is always accompanied by an increase in the size of the grains whatever the technique of development used [29]. The samples deposited at high temperature grow more slowly, which is equivalent to an annealing of the layer in formation, involving an increase in the size of the grains. The results obtained here agree well with the works of Chopra and Roth et al. [30-32] that showed that the grain size increases with the film thickness.

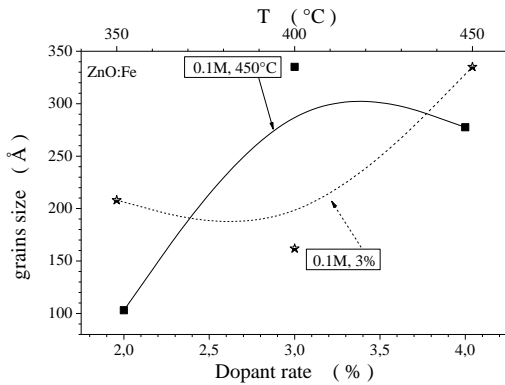


Fig.3. Variation of the estimated grain size with the doping rate and the temperature at 0.1M.

b. Optical Characterization

The transmittance spectra $T(\lambda)$ of ZnO:Fe films deposited on glass are shown on figures 4 and 5. Transmittance strongly depends on the substrate temperature and the doping rate. As mentioned above, at low doping rate (2%), the transmittance of the layers is relatively high for wavelengths higher than 500 nm. However, there are many causes for the transparency of the thin films deposited such as: the wavelength, substrate temperature, concentration of the solution and the reaction of decomposition of the droplets on the substrate. On the other hand, at high temperature, the transmittance is raised and depends slightly on the molarity and the doping rate. This indicates a complete thermal decomposition of the droplets involving the formation of a material close to the stoichiometry, which leads to layers of lower thicknesses. This is in good agreement with the results of Zaouk et al. [33] who showed that at higher temperatures, there is enough energy available for the thermal decomposition, solvent evaporates before the droplets reach the substrate and only the solid precursor reaches the substrate where thermal decomposition occurs. Consequently, the grown material is dense and the obtained films are relatively thin. That is also a consequence of the disappearance of the impurities following volatilization, at high temperature, of the secondary reaction products. The values found for the transmittance are about 45 to 70%, because the doping by iron reduces the transparency of the thin ZnO layers in the visible region.

c. Electrical Characterization

The electrical properties of the ZnO thin layers are of a considerable interest, in particular in the photovoltaic applications. Fig. 6 represents the variation of the electrical conductivity σ of the ZnO:Fe thin films with the doping rate. We can see

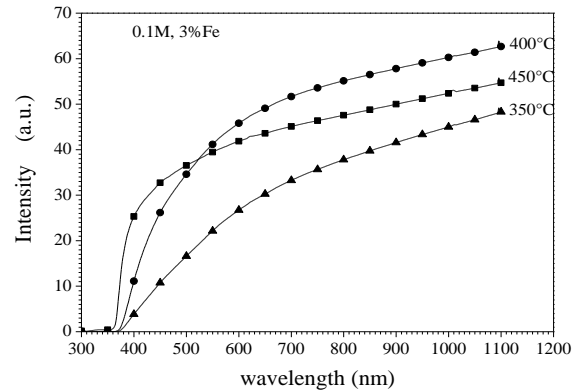


Fig.4. Variation of the optical transmittance with the wavelength for different temperatures of deposition at 0.1M and 3% (Fe)

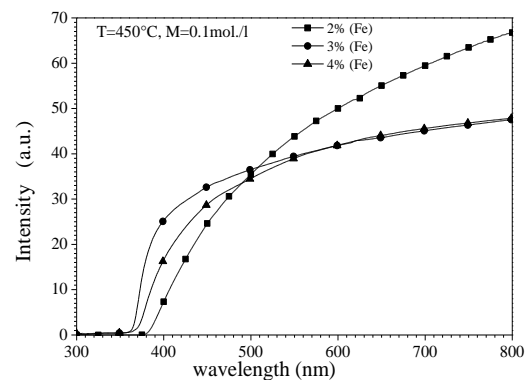


Fig.5. Variation of the optical transmittance with the wavelength for different doping rates at 0.1M and 450°C.

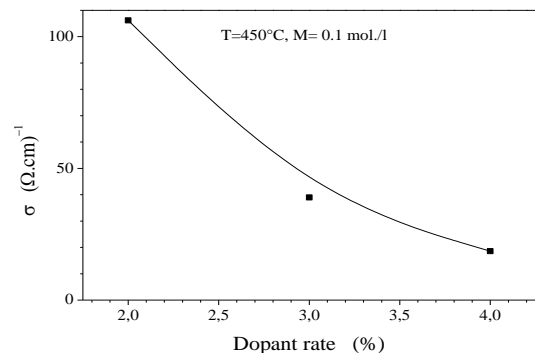


Fig.6. Variations of the electrical conductivity with the doping rate of layers deposited at 450°C.

that the electrical conductivity decreases with the doping rate. Figure 7 shows the variation of σ with the substrate temperatures T , for a fixed concentration and a doping rate (0.1M and 3% respectively). The electrical conductivity increases with substrate temperature. A resistivity of $2.9 \cdot 10^{-3} \Omega \cdot \text{cm}$ was found for films deposited at 450°C with an iron rate of 3%.

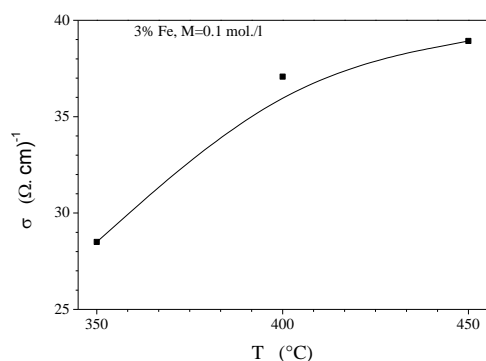


Fig.7. Variations of the electrical conductivity with the temperature of deposition at fixed concentration and doping rate.

4. Conclusion

ZnO:Fe semiconducting metal oxides were successfully synthesized by the spray pyrolysis method. The structural, optical and electrical properties of the Fe-doped ZnO thin films were investigated. The observed diffraction peaks are indexed to standard hexagonal wurtzite ZnO structure. No visible secondary phases for the doped ZnO thin films was found in the XRD patterns and the peaks were shifted to higher angles with the increase of Fe doping rate indicating the incorporation of doping atoms in the host matrix. The values found for the transmittance are about 45 to 70% in the visible. The electrical conductivity increases with substrate temperatures. Moreover, the temperature dependence measurements show that the electrical conductivity is controlled by thermally activated processes.

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