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Influence of Fe and Al Dopants on the Optical Properties of Zinc Oxide Thin Films Obtained by Spray Pyrolysis

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Abstract. An investigation has been done to study the influence of the Fe and Al doping concentration on the optical properties of zinc oxide thin films. A spray pyrolysis system was used to obtain ZnO:M films doped with Iron and Aluminum, using zinc acetate dihydrate, hydrated iron chlorate and hydrated aluminum chlorate, respectively. The temperature and the concentration were fixed at 450°C and 0.1mol/L, respectively. Our thin films deposed on glass substrate. UV-VIS spectrophotometer has been used for the layers characterization. The optical transmittance spectra showed that the 2% Al dopand improves the optical transmittance in the visible that the Fe dopand. Zinc oxide thin films is the n type semiconductor with direct optical band gap varied between 3.219-3.346eV for obtain the films in photovoltaic application. But the urbach energy of ZnO thin films undoped and doped by Iron and Aluminum is varied between 101–[illegible] meV.

1. Introduction

Zinc oxide (ZnO) is one of the most promising II–VI type semiconductors with an important direct wide band gap (3.3 eV at 300 K) [1-3]. Moreover, ZnO is available in abundance, low in cost and is environmentally safe because of its non-toxicity [4]. The properties of ZnO can be tailored by doping with cationic and anionic dopants like Al, Mn, Sn, Ag, Cu, Mg and Fe in order to make it suitable for several different applications in electronic, optoelectronic and piezoelectronique devices. [5-7]. Zinc oxide can be doped by Al and Fe which gives the transparent conductor oxide (TCO) and dilute magnetic semiconductors (DMS) respectively. These thin films have been worldwide scientific interest in II-VI. Investigation on DMSs was originally inspired by Ohno et al [8] for discovering the low temperature ferromagnetism in Mn doped GaAs with Curie temperature (Tc) around 110 K. After theoretical predictions of room temperature ferromagnetism (RTFM) in ZnO-based DMS systems by Dietl et al, [9-10] a number of groups investigated experimentally this phenomenon subsequently. However, the experimental results on Fe-doped ZnO systems were quite contradictory. X[illegible]uan et al. [11] synthesized the Fe-doped ZnO by using a coprecipitation method and found that it exhibits a weak ferromagnetic behavior at room temperature. X. L. Chen et al. [12] reported the observation of ferromagnetism of the Fe-doped tetra-needle ZnO whiskers at room temperature. [illegible] Y. Ahn et al. [13] fabricated the Zn0.97Fe0.003O compounds using the solid state reaction method. But, in recent years, transparent conductive oxide TCO is considered the most widely studied materials, is given in [14], basics to material physics of TCOs are discussed in [15], some structural investigation of TCOs was made e.g., in [16], preparation of TCOs was discussed in [17] and substitutes for the most popular transparent conducting oxide, namely ITO (indium-tin oxide), are listed in [18]. The optical transmittance measurements reveal that the transparency of ZnO films doped by Fe decreases with the increase of Fe concentration in ZnO [19]. ZnO films doped by Al has an edge over others for being a low cost and earth abundant material, low toxicity, stability in hydrogen plasma, higher optical transmission in UV-Visible range and lower electrical resistivity [20].

In last research, this films deposited several techniques such as chemical vapor deposition, laser ablation deposition and RF magnetron, but these methods require sophisticated equipment. But transparent conducting of zinc oxide thin films (ZnO) [21, 22] were prepared by spray pyrolysis method [22–28]; because this method is simple and inexpensive.

2. Experimental Procedure

In this work, one of the most important experimental parameters in thin films growth is the dopand concentration and substrate temperature, on amorphous glass substrate ZnO thin films were grown at fixed temperature (450°C) and fixed solution concentration (0.1°C).

The precursor solution was prepared by spray pyrolysis technique. In our work, solution was prepared by mixing zinc acetate dihydrate, distilled water; aluminum chlorate and iron chlorate were starting materials, solute, dissolvent and dopand source, respectively. These dopand source for prepared the transparent conductor oxide (TCO) and dilute magnetic semiconductor (DMS) materials respectively.

According to a certain proportion, zinc acetate and dopand source were first dissolved in distilled water at room temperature. The dopand source concentration (Al and Fe) were 0%, 2%, 3% and 4%. Before doing something, the substrates were cleaned thoroughly. The transmittance and absorption spectra were recorded by an UV-visible spectrometer.

The relation between transmittance and absorption is:

$$T = (1 - R).\exp(-\alpha.d) \quad (1)$$

T is the transmittance, α is the absorption, d is the thickness, R is the reflectance negligible in our calcule.

The optic band gap of thin films calculated by following relation:

$$(\alpha h\nu)^2 = \alpha(h\nu - Eg)^{1/2} \quad (2)$$

Where:

Eg: Optical gap energy, hυ: photon energy.

The formula (3) determining an important parameter that characterizes the disorder of the material is the Urbach energy (E_{Urb}) By law expression Urbach with the absorption coefficient is of the form:

$$\ln(\alpha) = \alpha_0 \ln(\frac{h\nu}{E_{Urb}}) \quad (3)$$

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3. Results and Discussion

Figure 1 presents the transmittance spectra of Aluminum and iron doped zinc oxide at different dopand concentration (0%, 2%, 3% and 4%) with fixed temperature (450°C) and fixed solution concentration (0.1mol/l). The curves showed that the transmittance of thin films decreases with an increase of the dopand percentages. This decrease of the transmittance of thin films doped by Al and Fe grown from high atomic percentage may be due to the degradation in the crystalline of the films. The transmittance in the doped samples at 2% to Aluminum is higher than the other thin films doped at 0%, 3% and 4% with aluminum. The same observation in the case of the doped samples at 2% to iron is higher than the other thin films doped at 0%, 3% and 4% with iron. The transmittance of thin films of ZnO doped with Aluminum is higher than the transmittance of thin films of ZnO undoped and doped with Iron because the iron atoms is changed the color of the thin films deposited from transparent to brown. But the aluminum atoms keep the transparence of thin films.

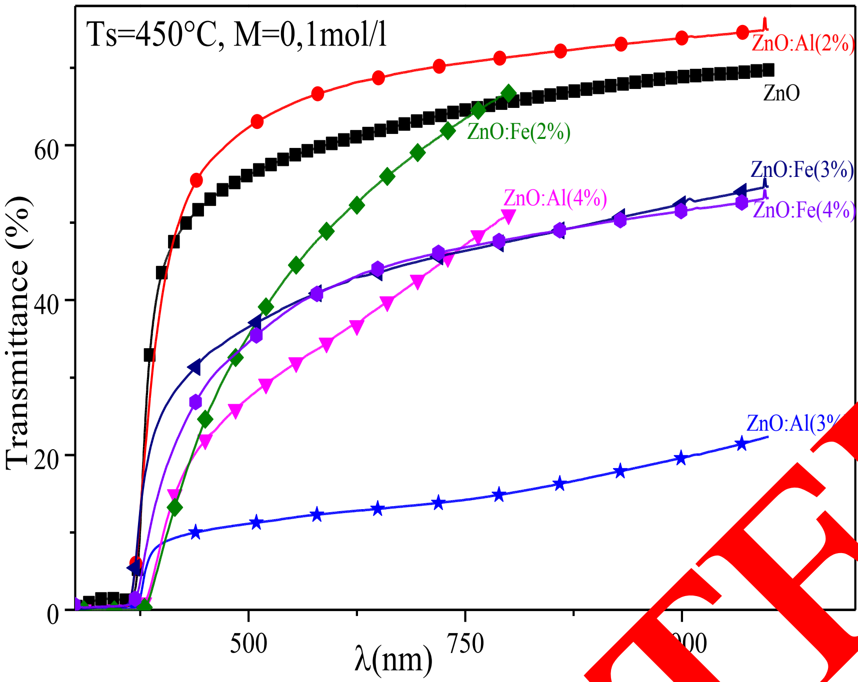

Figure 1. Transmittance spectra of zinc oxide doped with Aluminum and iron.

The values of the transmittance allowed us to determine the optic gap energy and the Urbach energy on our thin zinc oxide films deposited with different dop and concentrations, using two formulas (2) and (3) respectively.
The optic gap energy determined by using the curve ($\alpha h\upsilon$) various with photonic energy ($h\upsilon$), Eg obtained when $(\alpha h\upsilon)^2 = 0$, Figure 2.

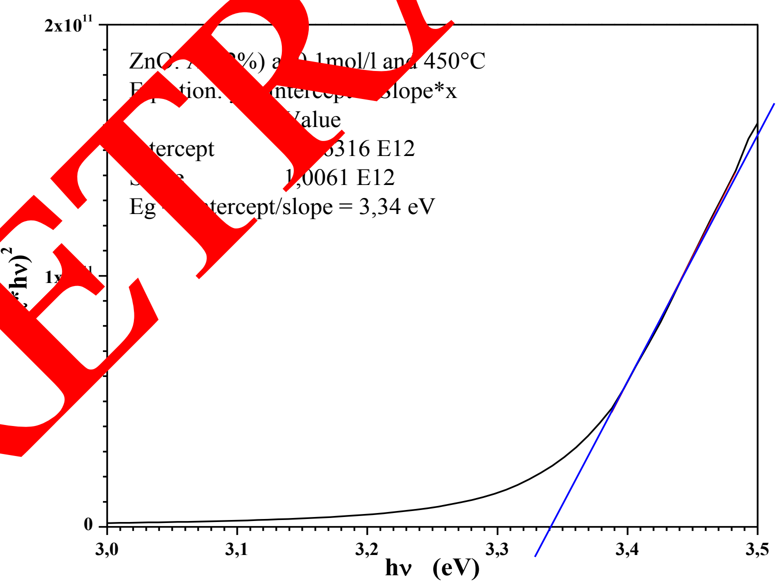

Figure 2. Determined the optic gap energy for ZnO: Al (2%) thin film.

The urbach energy determined by plotting the log (α) various with photonic energy, when urbach energy is the inverse of curve slope, Figure 3.

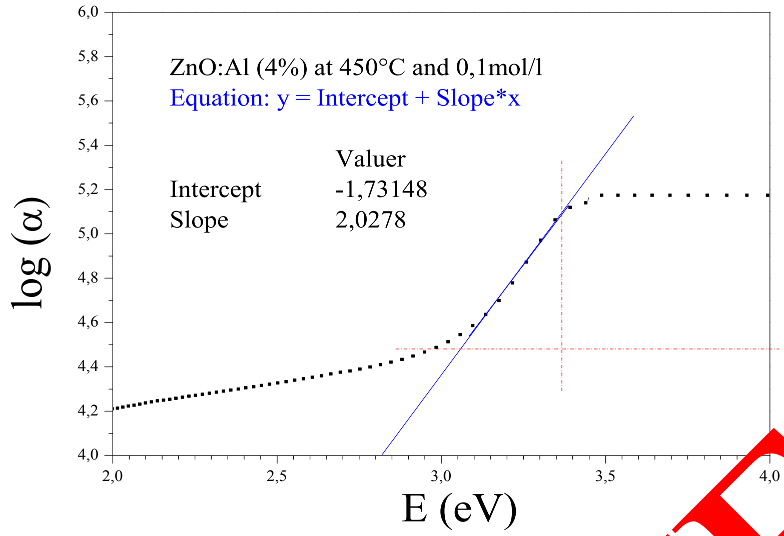

Figure 3. Determined the Urbach energy for ZnO:Al.

The various values of optical gap energy and urbach energy shown in Figure 4 and 5 with different dopand concentrations, we can observe that the energy gap for Al doping is more significant when the thin films of ZnO doped at 2%. But for iron doping, the large energy gap was presented when the thin films of ZnO doped Fe at 3%.

The optical gap energy to the thin films of zinc oxide doped at 3% iron is 3.317 eV, it is larger than the other thin films doped by Fe at 0% 2% and 4% with iron. Except that the doping with Al 2% of the energy gap is equal 3.346 eV, it is larger than other thin films doped at 0%, 3% and 4% with Aluminum.

From Figure 4, it is observed that the optical gap energy for thin films doped by Al at 2% greater than the other doping rate. But a decrease after 2% is determined, this decrease shows that the doping by Al gives thin films with smaller optical gap than the ZnO undoped and doped by Fe.

The Urbach energy is augmented to more than 4% doping of Al and Fe with respect to the percentage of other dopand.

In the Figure 5, it is observed that the Urbach energy for thin layers doped by Fe and Al augmented to 2% then decreased at 3%, but for the percentage 4% the Urbach energy is very greater compared to the other values.

In Figure [illegible] we are presented the growth speed of our thin films. It is observed that the decrease in the growth speed for the Zinc oxide thin films doped with Aluminum up to 2% and then an increase in the percentage 3% and 4%, on the other hand for the Zinc oxide thin films doped by Fe, it is considered that an increase at the rate 2% then a decrease to 3% then an increase top 4%. This difference can be explained by several conditions such as: the method of preparation which can cause large difference in level, to recover the same temperature require a longs time, also the position of the substrate on the hate plate, times the drops of the solution fallen on the substrate with no decomposition, and on other hand the percentage of the dopants varies the values of the growth speed.

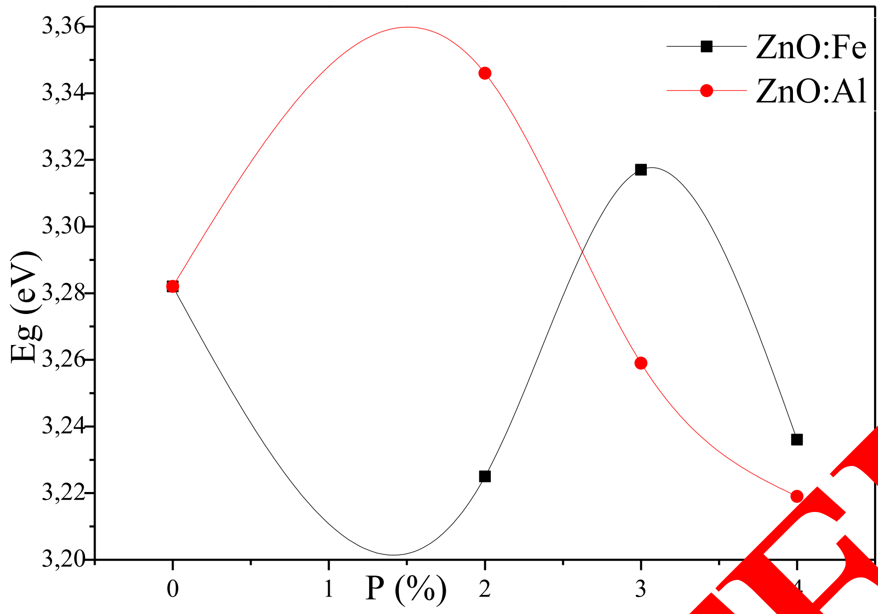

Figure 4. Optical gap energy as a function of the dopants rate in the thin films.

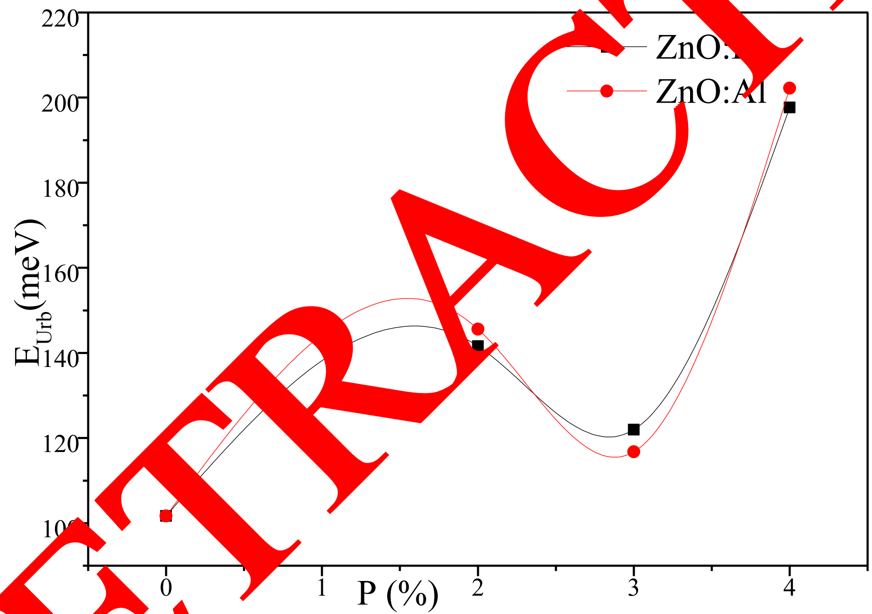

Figure 5. Urbach energy E_{Urb} as a function of the dopants rate in the thin films.

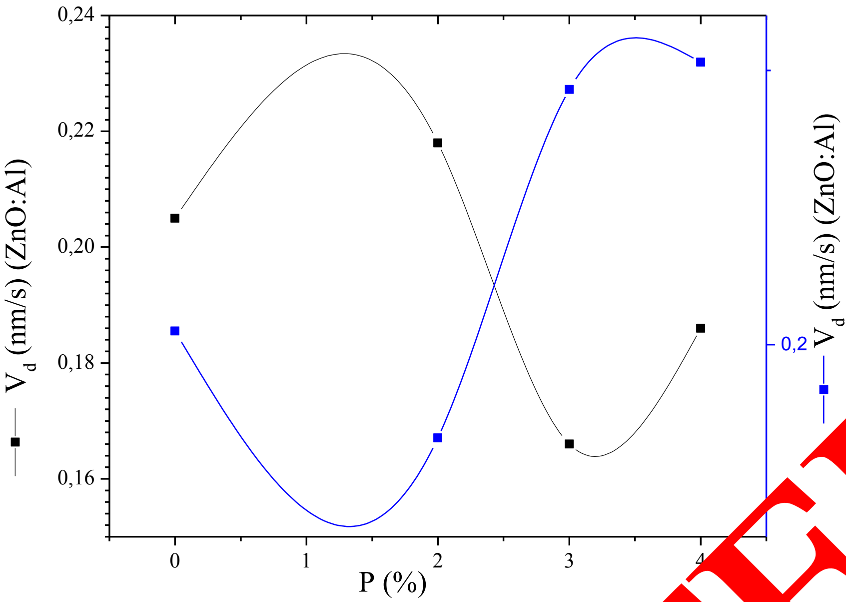

Figure 6. Growth speed as a function of percentage of the dopants for the thin layers of ZnO:Al and ZnO:Fe.

Conclusion

In our work, the transparent conductor oxide (TCO) and dilute magnetic semiconductor (DMS) for zinc oxide doped by Aluminum and iron, respectively, were obtained by spray pyrolysis technique; it is the inexpensive method with the other methods. The transmittance of the ZnO:Al at 2% concentration is very high for other layer at different dopand concentration and high optic gap energy about 3.35 eV. The optical band gap lies in the range 3.1-3.35 eV, showing an improvement in transparency with dopand concentration for window application at 450°C substrate temperature, whether, for zinc oxide thin films doped with aluminum or iron. ZnO thin films are used in various applications due to their high optical transmittance in the visible light region about 75% for ZnO: Al (2%). The growth speed varies with the variation in the percentage of dopants of the thin films of ZnO:Al and ZnO:Fe.

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