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## Influence of Al Dopant on the Optical and Electrical Properties of Zinc Oxide Thin Films Prepared by Spray Pyrolysis

A. Alaeddine, I. Rachidi, F. Bahsoun, Y. Mohanna, O. Bazzi and F. El Haj Hassan  
Laboratoire de Physique des Matériaux (LPM), Facultés des Sciences I, Université Libanaise,  
El-Hadath, Beyrouth-Lebanon

**Abstract:** Pure and aluminum doped ZnO transparent thin films were prepared by spray pyrolysis. ZnO thin films are formed by decomposition of  $(\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O})$  to ZnO. The aluminum doping, Al/Zn of 4/96, was achieved by the addition of  $\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$  in methanol solution of the chemical complex  $(\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O})$ . The films are transparent (> 80% optical transmission) in the near UV, VIS and near IR ranges. X-ray diffraction analysis indicates that the crystallites of both ZnO and ZnO:Al thin films are preferentially oriented along the c-axis, [002] direction of the hexagonal compact structure of type. The electric properties (electrical conductivity and electrical mobility) and the optical property (transmittance) of aluminum doped ZnO films have been measured. The results have been compared to those obtained with undoped ZnO thin films. The doping modifies the structure and the morphology of the obtained films and it increases the optical transmittance and the electrical conductivity.

**Key words:** Thin films, optical transmittance, electrical conductivity, gap energy

### INTRODUCTION

ZnO thin film is technologically important due to the many advantages over other transparent conductive oxides thin films and especially to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and of its low price (Major *et al.*, 1986; Studenikin *et al.*, 1998; Sahay and Nath, 2008).

Pure ZnO thin films are not stable against corrosive environments (adsorption of dioxygen in the films decreases the electrical conductivity and also modifies the surface morphology. These films become more stable by doping them especially with aluminum (Jiménez-González *et al.*, 1998).

These films have a range of optical and electrical properties which make them suitable for a variety of applications (Ben Ayadi *et al.*, 2007; Paraguay *et al.*, 2000; Kwon *et al.*, 1995; Ambra *et al.*, 1992). Moreover, doped zinc oxide films have many interesting applications (Minami *et al.*, 2007). Many researchers have been done about doped ZnO films and the influence of the dopants on the microstructure and growth of these films (Chakraborty *et al.*, 2008; Hu and Gordon, 1992; Van Heerden and Swanepoel, 1997; Krunk and Mellikov, 1995; Messaoudi *et al.*, 1995; Park *et al.*, 1997; Nakada *et al.*, 1995; Labeau *et al.*, 1992) and on their

electrical and optical properties (De Merchant and Cocivera, 1995). Typical dopants that have been used belongs to the group IIIa elements of the periodic table (B, Al, Ga, In) (Seeber *et al.*, 1999).

To obtain the doped Al-ZnO films, we have used a spray pyrolytic system because this technique has proved to be simple, reproducible and inexpensive method (Kruncks *et al.*, 1999; Paraguay *et al.*, 1999).

It was found that growth temperature and material doping level have very strong effects on the structural, electrical and optical properties of sprayed ZnO films.

In this study, we present the influence of aluminum dopant on the optical properties (in the near UV, VIS and the near IR) and on the electrical conductivity of the ZnO films. We will discuss the modifications of the crystalline being introduced by aluminum doping.

### MATERIALS AND METHODS

Pure and aluminum doped zinc oxide films were prepared in a Spray Pyrolysis Technique (SPT) (Seeber *et al.*, 1999). The spraying solution was 0.2 M zinc acetate  $(\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O})$  in a de-ionized water. The doping was achieved by adding  $\text{AlCl}_3$  to the spraying solution (a mixture (1:3) of methanol and de-ionized water) in a concentration of 4%.

The glass substrate was placed at 28 cm from the nozzle and the growth temperature is kept constant at 440°C and was controlled within ±5°C through a thermocouple as a sensor for the temperature control. The solution flow rate and gas pressure was kept constant at 8.33 L sec<sup>-1</sup>. Nitrogen was used as the carrier gas.

The growth temperature was chosen on the basis of previous results confirming that ZnO films grown at a temperature of the order of 440°C have the best structural and optical properties.

The samples are annealed at 400°C for 1 h before making measurements, in order to achieve structure homogeneity.

X-ray diffraction (XRD) patterns of the sprayed films were recorded using a Siemens diffractometer D-5000 Kristalloflex with monochromatic Cu K<sub>α</sub> radiation and it is used to determine the crystal structure.

The optical transmittance spectra were recorded in the wavelength range of 300-1200 nm on a Cary 5G UV-VIS-NIR Spectrophotometer.

The surface morphology of the films was examined by scanning electron microscopy (SEM of type JEOEL 6400).

Electrical conductivity of the films was measured by the four-point method using Van der Pauw technique with a KEITHLY bench measurement set.

**Structure and morphology analysis:** We employed the X-ray diffraction technique to get a first impression of the possible orientation of crystallites of different prepared samples to compare the effect of the dopant on the thin film structure.

It is well known that if the (002) peak is very strong; the grains are strongly oriented in the c-axis in the hexagonal structure, i.e., perpendicular to the plane of the substrate (Jiménez-González, 1998; Ma, 1996).

Figure 1a and b show X-ray diffraction patterns of undoped and Al doped ZnO films which exhibit a strong c-axis orientation perpendicular to the substrate.

To the different crystal orientations. It can be seen that the crystalline properties of the films doped with Al is smaller than that of pure ZnO films as shown by the smaller intensity of the diffraction peaks and the decrease of the ratio peak intensity/background signal.

For Al concentration of 4%, the films indicate a preferential growth along the (101) direction and the relative intensity of the I<sub>002</sub>/I<sub>101</sub> decreases. This relative intensity decreases from I<sub>002</sub>/I<sub>101</sub> ≥ 10 (found for undoped films) to I<sub>002</sub>/I<sub>101</sub> ≈ 3 (for a doping level 4% Al).

Thus conclude that the crystallites of pure ZnO films are strongly oriented along c axis in the type hexagonal structure perpendicular to the plane of the substrate. The peak (002) remains strong in the ZnO and the Al doping ZnO films.

Figure 2a and b obtained by Scanning Electron Microscopy (SEM), show that there is a decrease in the crystallite size when the zinc oxide is doped with aluminum and the surface becomes smoother. This observation is in good agreement with the study of Islam *et al.* (1996).

**Optical results:** Transparency and homogeneity of pure and aluminum-doped ZnO thin films can be tested through optical transmittance measurements.

The optical transmittance spectra for undoped and Al-doped ZnO films are presented in Fig. 3a and b in the wavelength range (near UV, VIS and near Infra-red: 300-1200 nm).

From these curves, we notice that the transmittance curves of pure and aluminum doped ZnO films are very sharp in the UV band edge region. An optical transmittance higher than 80% was detected in the near UV, visible and near infra-red region of spectra.

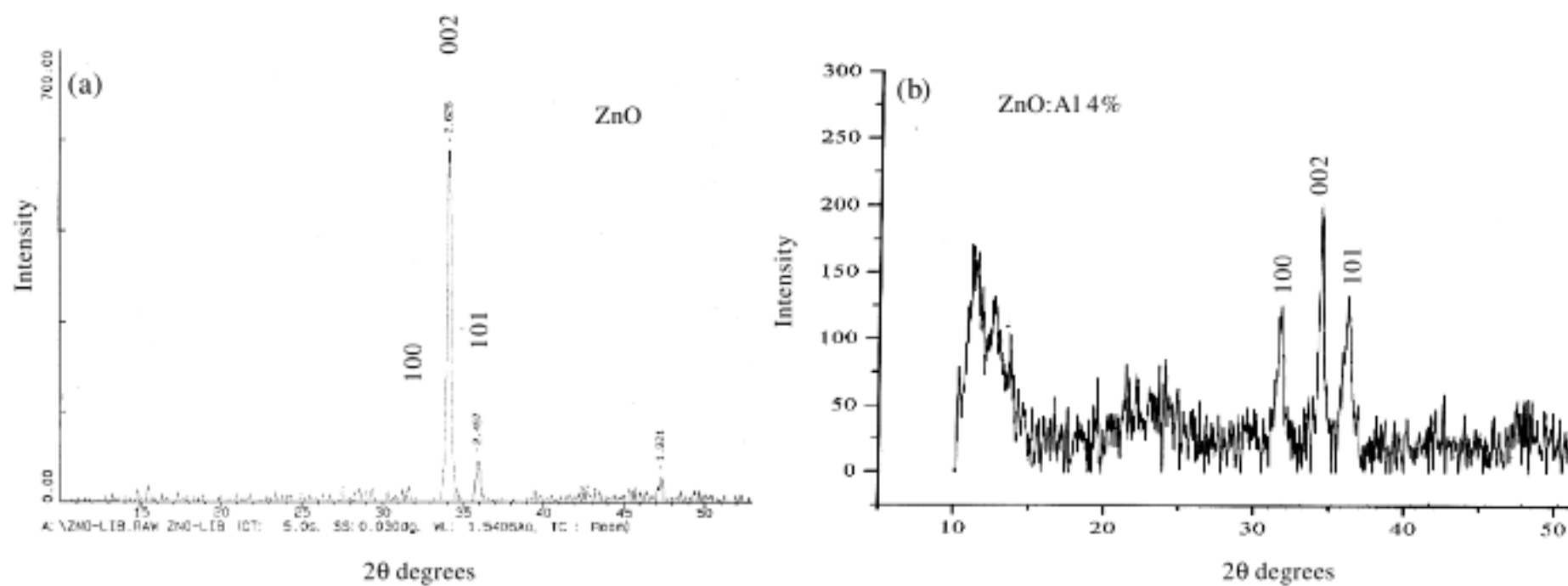


Fig. 1: X-ray diffraction patterns of : (a) undoped and (b) Al doped ZnO films

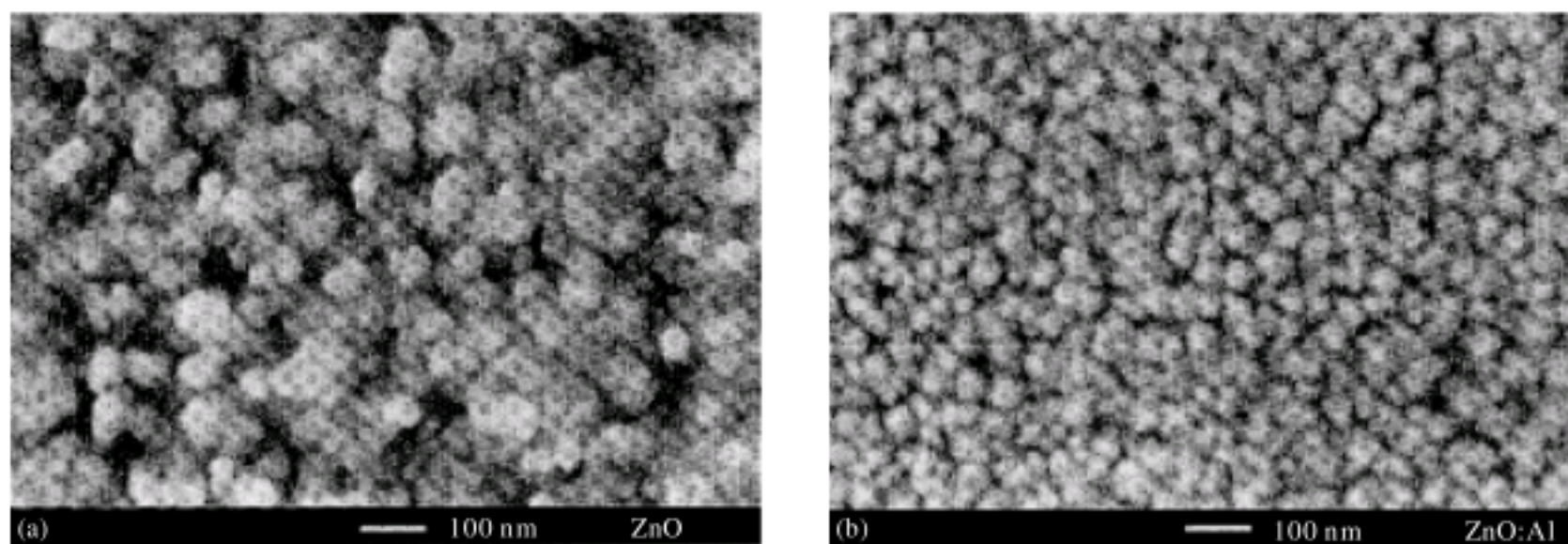


Fig. 2: Scanning Electron Microscopy (SEM), (a) undoped and (b) Al doped ZnO films

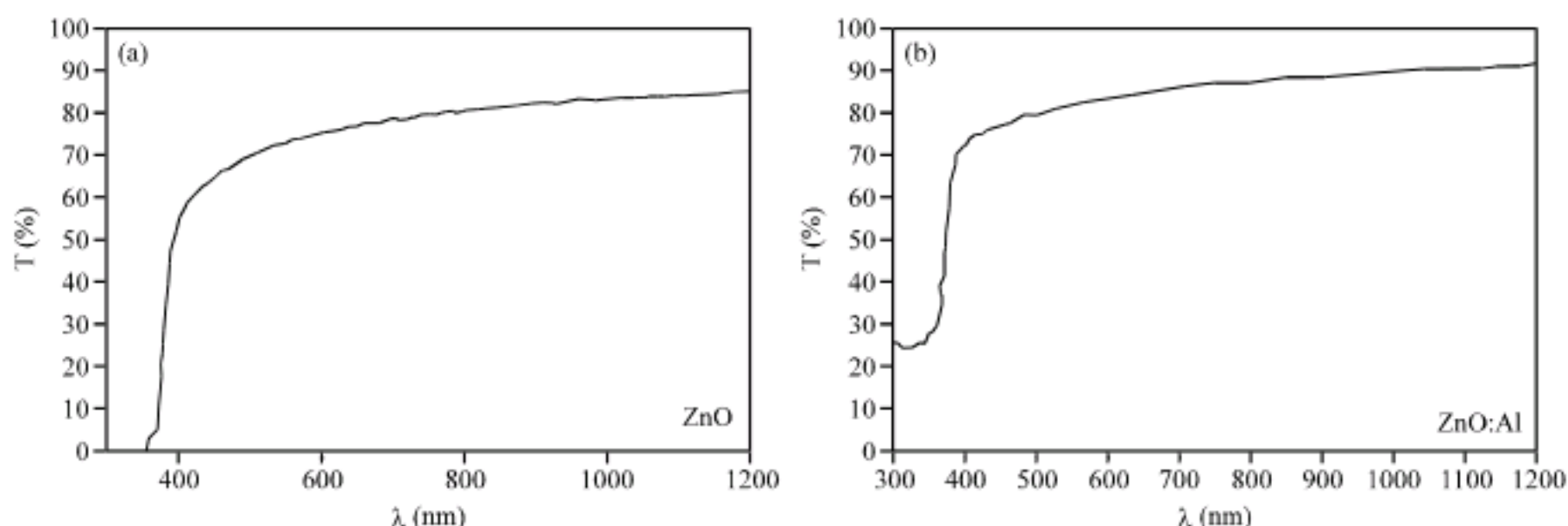


Fig. 3: The optical transmittance spectra (a) undoped and (b) Al doped ZnO films

The optical transmittance for the aluminum doped films (4%) is higher than the transmittance for the pure ZnO films; this result agrees with the study of Jiménez-González *et al.* (1998).

**Band gap determination:** To determine the energy gap, most authors use the model for direct interband transitions:

$$\alpha hv = C (hv - E_g)^{1/2}$$

where,  $hv$  is the photon energy,  $\alpha$  the absorption coefficient,  $E_g$  the band gap energy and  $C$  the coefficient of proportionality. This model may not be suited to wide band gap materials (Studenikin *et al.*, 1998). In this approximation  $(\alpha hv)^2$  should be a linear function of  $hv$  for high frequencies.

The value of the band gap which corresponds to the threshold of optical absorption is obtained by extrapolation of the tangent on the curve drawn in the zone of strong absorption (Fig. 4a, b).

The obtained band gap is in the order of 3.30 eV for undoped ZnO films and in the order of 3.32 eV for Al

doped ZnO 4%. This result is in agreement with the values 3.3 eV obtained by Jiménez-González *et al.* (1998) and 3.39 eV obtained by Seeber *et al.* (1999) for undoped ZnO films and approximately the same values for doped aluminum ZnO films.

Thus, we observe that aluminum doping increases the band gap of ZnO by a maximum of two hundredths of eV. Apparently it is not a significant increase in the band gap. This explains the results, the increase in conductivity is due to the conduction electrons obtained by ionization of the introduced donor levels.

**Electrical results:** To express and evaluate the film receptivity  $\rho$ , van der Pauw technique (Mzerd *et al.*, 1992) was used at room temperature. In addition to obtain better results the electrical contacts were prepared by silver print.

We obtain a resistivity  $\rho = 10^4 \Omega \text{ cm}$  (a conductivity  $\sigma = 10^{-4} (\Omega \text{ cm})^{-1}$ ) for the pure ZnO films and for 4% doped aluminum ZnO films we obtain a resistivity  $\rho = 300 \Omega \text{ cm}$  (a conductivity  $\sigma = 3.3 \cdot 10^{-3} (\Omega \text{ cm})^{-1}$ ).

This increase in electrical conductivity brought by the aluminum doping, can be explained as follows: The

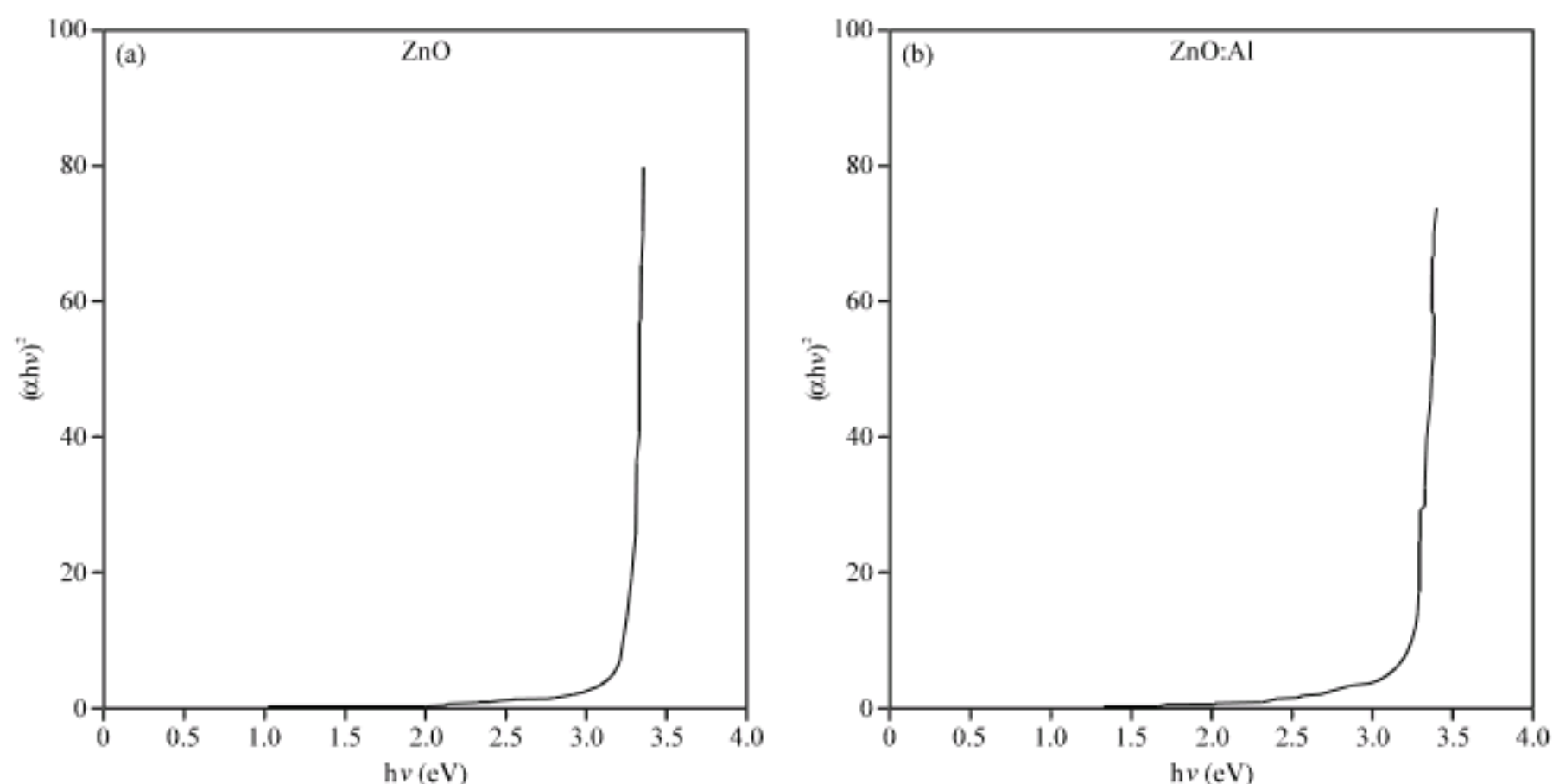


Fig. 4: The  $(\alpha hv)^2$  versus  $h\nu$  curve of, (a) undoped and (b) Al doped ZnO films

concentration of the free charge carriers in ZnO increases by the aluminum doping because aluminum has one valence electron more than zinc. We may consider that an aluminum atom substitutes the zinc atom or it occupies interstitial sites. In both cases the added aluminum dopant incorporates into the crystal and acts as donor dopant.

### CONCLUSION

The two kinds of films pure and Al doped ZnO films were polycrystalline with the ZnO hexagonal type structure. For the ZnO aluminum films, it can be observed that the film growth is strongly (002) oriented, while the (101) orientation shows an increase in the doped films.

It has been also shown that aluminum doping enhances the electrical conductivity and the optical transmittance of ZnO films.

The band gap energy and the receptivity  $\rho$  for Al doped ZnO and pure ZnO films were also investigated.

### ACKNOWLEDGMENTS

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