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# Effect of thermal annealing on ZnO:Al thin films grown by spray pyrolysis

A. El Manouni[a,b], F.J. Manjón[a,*], M. Perales[a], M. Mollar[a], B. Marí[a], M.C. Lopez[c], J.R. Ramos Barrado[c]

[a] *Dept. de Física Aplicada, Universitat Politècnica de València, Camí de Vera s/n, E-46022 València, Spain*
[b] *Dept de Physique, Université Hassa II, FST 20650 Mohammédia, Morocco*
[c] *Dept. de Física Aplicada I, Universidad de Málaga, Av. de Cervantes 2, E-29071 Málaga, Spain*

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**Abstract**

We report the effect of thermal annealing in air on the structural and optical properties of undoped and aluminium-doped (1%–4%) zinc oxide (AZO) thin films, grown by the spray pyrolysis technique on quartz substrates. Films were characterized by X-ray diffraction, low-temperature photoluminescence, electrical resistivity, and Raman spectroscopy after annealing at temperatures between 500 and 900 °C. Annealing in air improves the long-range order crystalline quality of the bulk crystals, but promotes a number of point defects in the surface affecting both the resistivity and the photoluminescence.


*Keywords:* Zinc oxide; II–VI semiconductors; Wide bandgap semiconductors

## 1. Introduction

ZnO is a semiconductor with a wide bandgap of about 3.37 eV at room temperature (RT), which can be used in a number of optoelectronic devices [solar cells, UV photodetectors, light emitting diodes (LED), laser diodes (LD), and thin film transistors] due to their excellent electrical and optical properties [1,2]. Undoped ZnO has a high n-type conductivity due to defects like oxygen vacancies ($V_O$) and Zn interstitials ($Zn_i$), which form donor levels [3]. In order to improve the structural, optical and electrical properties, ZnO can be doped with a wide variety

* Corresponding author. Tel.: +34 96 3877000x75287; fax: +34 96 387 71 89.
*E-mail address:* fjmanjon@fis.upv.es (F.J. Manjón).

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of ions depending on the application fields [4,5]. In particular, group IIIa elements (Al, Ga, In) are used to improve the electrical conductivity. Furthermore, they improve also the thermal stability of films. We had chosen Al as a dopant because it acts as a donor when it occupies a substitutional position for $Zn^{2+}$ cation or an interstitial position in the ZnO lattice [6]. Among the several techniques used to obtain high quality undoped and doped ZnO thin films, we have used the spray pyrolysis method that has the advantages of low cost, easy-to-use, safe and efficient route to coat large surface areas in mass production.

In a previous paper, we studied the effect of Al doping in ZnO grown by spray pyrolysis [4]. In the present work, we report the effect of thermal annealing in air atmosphere on structural, optical, and electrical properties of Al-doped ZnO thin layers (AZO) grown on quartz substrate by spray pyrolysis technique.

## 2. Experimental

As-grown ZnO and AZO thin films were prepared by the spray pyrolysis technique [4,7]. Annealings in atmosphere air were performed inside a tubular oven at different temperatures up to 900 °C. The film crystalline quality was analysed by an X-ray diffractometer with Cu K$\alpha$ radiation and by Raman spectroscopy, as in Ref. [4]. Electrical resistivity was determined from the sheet resistance measurement by a four-point probe method, and optical properties were investigated by low-temperature photoluminescence (PL) at 19 K, as in Ref. [4].

## 3. Results and discussion

All undoped ZnO and AZO thin films were polycrystalline with a hexagonal wurtzite structure. X-ray diffraction (XRD) results (not shown here) indicate that the films exhibited a preferred (002) orientation with the intensity of (002) peak decreasing with the increase of aluminium doping [4]. It was observed and discussed that there was a severe decrease of the film crystalline quality for Al concentrations higher than 2% [4]. Thermal annealing on air improved the crystalline quality of the films by the increase of the (002) peak intensity and the decrease of the (002) peak width.

Figs. 1(a) and (b) show the Raman spectra of the undoped ZnO and AZO thin films in as-grown samples and after annealing at 900 °C, respectively. It can be observed in Fig. 1(a) that, similarly to the Raman spectra in Ref. [4], the increase of the Al concentration leads to a decrease of the $E_2$(high) mode intensity, and to an increase of the $A_1$(LO) mode. The overall increase of a broad band covering the whole spectrum evidences the presence of an amorphous phase in some as-grown samples with increasing Al doping. The Raman spectra of annealed samples are rather similar and exhibit a high intensity of the $E_2$(high) mode and a small intensity of the $A_1$(LO) mode, thus suggesting a similar crystalline quality of all the annealed films after annealing at 900 °C.

Fig. 2 shows the behaviour of the resistivity in undoped ZnO and AZO thin films at different annealing temperatures. The resistivities of all samples decreased by two orders of magnitude after annealing to 500 °C independently of the doping level. The AZO sample with 1% Al concentration showed the lowest resistivity of all as-grown samples [4], and retains the lowest resistivity after annealing in air below 700 °C being the lowest value of resistivity $5.44 \times 10^{-3}$ Ω cm after annealing at 500 °C. Curiously, the resistivities of all samples increased over their values in as-grown samples after annealing above 700 °C, showing almost the same resistivity for annealing temperatures above 800 °C independently of the doping level.

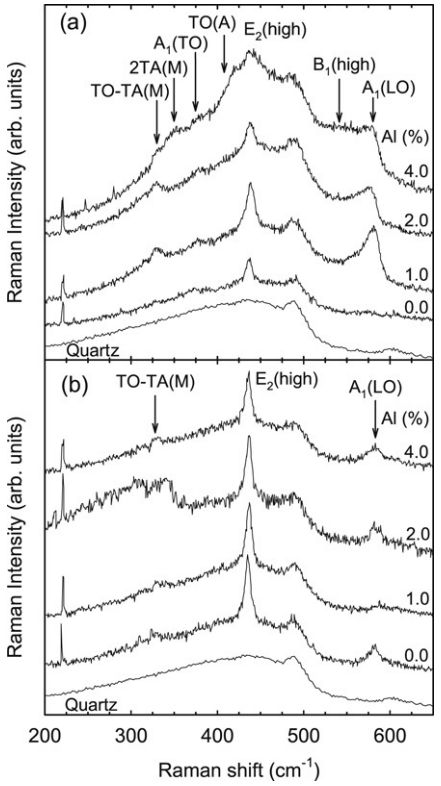


Fig. 1. Room temperature backscattering Raman spectra of as-grown undoped ZnO and AZO thin films (a) and after annealing at 900 °C (b).

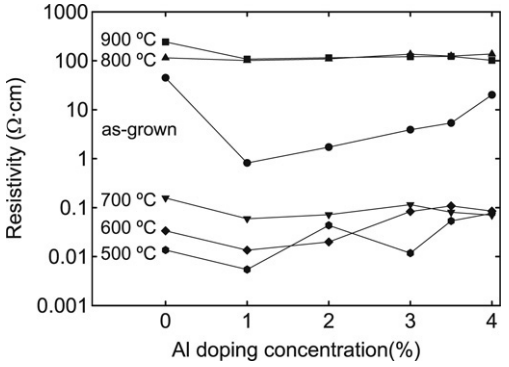


Fig. 2. Electrical resistivity of undoped ZnO and AZO thin films deposited on quartz as a function of Al concentration for different annealing temperatures.

Fig. 3 shows the low-temperature PL spectra of undoped ZnO and AZO thin films in as-grown and annealed samples. In the spectra there is a small blue band around 400 nm (3 eV) that is an artefact due to the undesired scattering of the laser light onto the Al foil used to sustain samples inside the cryostat. The as-grown undoped ZnO thin film exhibits two PL peaks in the UV

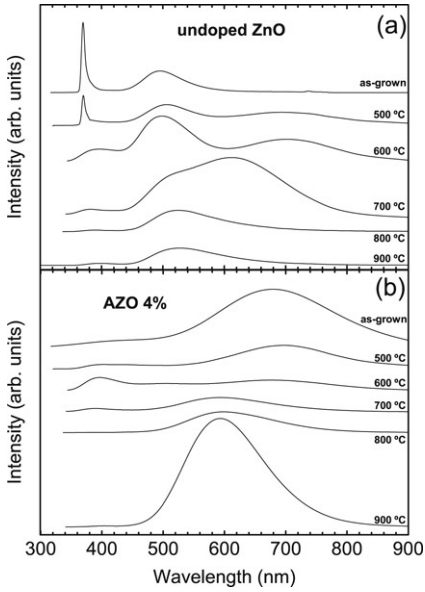


Fig. 3. Low-temperature photoluminescence spectra of undoped ZnO films (a), and AZO thin films with 4% Al concentrations (b) plots correspond to as-grown samples and samples annealed at different temperatures.

(369 nm) and blue–green regions (500 nm) [4]. A decrease of the UV excitonic peak intensity and the appearance of red emission near 700 nm (1.8 eV) are observed after annealing at 500 °C. Annealing at 600 °C led to the disappearance of the excitonic emission and to the increase in intensity of the green and red emissions in the undoped ZnO film. After annealing at 700 °C, the main feature is the redshift of the green emission and the blueshift of the red emission giving a spectrum with a broad band composed of two peaks. Finally, after annealing at temperatures above 800 °C the red emission disappears and appears only a broad green band near 520 nm that it is broader than the blue–green band near 500 nm of the as-grown undoped ZnO sample. A similar decrease of the excitonic peak and increase of the green emission in undoped ZnO films under annealing in atmospheric oxygen has been recently observed [8].

As-grown AZO samples exhibited only a broad red band near 700 nm [4]. Annealing at 500 and 600 °C causes an increase (decrease) of the intensity of the red band in the AZO sample with 1% Al (4% Al). In the AZO sample with 2% Al, the red band maintains its intensity after annealing at 500 and 600 °C. Besides, annealing at 600 °C leads to the formation of a small green band also in the doped samples. Annealing above 700 °C causes a large blueshift of the red band in all the Al-doped samples, like in the undoped sample, and the appearance of a yellow–orange band centred near 590 nm that increased in intensity on increasing the annealing temperature above 700 °C.

Raman spectra allow us to discuss the structural behaviour of the undoped and AZO thin films with annealing temperature. The rather small intensity of the $E_2$(high) mode in the Raman spectra of as-grown samples suggests a rather poor quality of the as-grown films that decreases with increasing the Al doping in agreement with XRD results [4]. According to our Raman measurements in as-grown films, the AZO film with 1% Al shows the best crystalline quality. At present, we have no clear explanation for the increase of crystalline quality of AZO films with small doping levels with respect to undoped ZnO films. The quality of the doped crystals

decreases for higher doping levels as revealed in the decrease of the $E_2$(high) intensity and the increase of a broad band covering the whole spectra that can be associated to amorphous ZnO appearing in some films. After annealing to 900 °C, the $E_2$(high) mode increases in intensity in all samples and the broad band covering the whole spectrum disappears, thus indicating an overall improvement of the crystal quality with no presence of amorphous phases in annealed samples. This result agrees with our XRD measurements showing an overall improvement of the crystal quality of the bulk film on annealing. The presence of increasing amorphous ZnO with increasing Al doping in as-grown samples suggests that disorder-activated Raman scattering (DARS) can also be seen. This is in fact what is observed in the samples with 3.5 and 4% where a plateau can be observed around 550 $cm^{-1}$ that can be attributed to the presence of the inactive $B_1$(high) mode due to DARS [9].

Despite Hall measurements are desirable to analyze the effects of thermal annealing on fundamental electronic mechanisms in AZO layers, we think that the decrease in electrical resistivity in as-grown doped films with respect to the undoped one can be interpreted mainly by the increase of free carrier concentration provided by the $Al^{3+}$ ions acting as donors when incorporated in substitutional or interstitial positions [4]. The increase in resistivity for concentrations above 1% Al concentration was interpreted by the decrease of carrier concentration in the films due to formation of electron traps that developed for high doping concentrations [4]. We think that the decrease of the resistivity of undoped and doped samples annealed at 500 °C is due to the improvement of crystal quality and the consequent increment of both carrier concentration and mobility. Mobility is enhanced by the removal of bulk crystal defects and the increase of grain size [10]. The increase in the carrier concentration could be attributed to the ionisation of oxygen vacancies ($V_O$) followed by oxygen annihilation from the ZnO crystals and by desorption of oxygen in the grain boundaries which act as traps for the carriers [11]. An activation of Al donors between 500 and 650 °C is suggested by Shishiyanu et al. from PL measurements [12]. However, the similar resistivity increase in all our samples above 500 °C indicates that there is no activation of Al donors or that the activation of Al donors is compensated by the creation of new acceptors above 500 °C. Furthermore, the increase in resistivity of all samples above 500 °C suggests the formation of acceptor levels or the removal of the native donor levels above this temperature. The increase in resistivity could be explained by a reduction of Zn interstitial ($Zn_i$) concentration causing the decrease of the carrier concentration. The reduction of $Zn_i$ at elevated temperatures can be due to the evaporation of Zn due to the high vapour pressure of zinc [13]. Other explanation for the increase in resistivity is the creation of a number of $V_{Zn}$ or $O_{Zn}$ acceptors at high annealing temperatures.

As regards the behaviour of the PL signal, in our previous work we concluded that the lack of excitonic UV emission in as-grown AZO samples evidences the degradation of the crystalline quality of the surface in the doped films with increasing Al doping [4]. In a similar way, the decrease of the excitonic UV emission in undoped ZnO films after annealing evidences the degradation of the crystalline quality of the surface after annealing in atmospheric air. This degradation of the surface quality with annealing in air is consistent with the appearance of a new red band around 700 nm in undoped ZnO films after annealing at 500 and 600 °C and the subsequent appearance of a green band above 700 °C. Since similar red bands are present in as-grown AZO films and similar yellow bands are present in annealed AZO films, we conclude that annealing promotes the formation of a new surface defect in undoped ZnO films similar to the one caused by Al doping, and that annealing above 700 °C promotes a new surface defect in undoped (doped) films responsible for the green (yellow) band and the increase of resistivity above the value for as-grown thin films.

## 4. Conclusion

The effect of thermal annealing in air in undoped ZnO and AZO thin films grown by the spray pyrolysis technique on quartz substrates is reported. X-ray diffraction and Raman scattering show that films exhibit a better crystallization after thermal annealing. The resistivity decrease for annealing at 500 °C but increases for annealing at higher temperatures. No activation of Al donors has been observed after annealing in air. Furthermore, high-resistivity films are obtained after annealing at 800–900 °C. The PL signal shows drastic changes after thermal annealing in air that closely match to the changes in resistivity. We think that the annealing in air improves the bulk crystal quality of the thin films but with a lower surface quality due to the promotion of surface defects responsible for the changes observed in resistivity and PL emission.

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