Transparent and conductive Al/F and In co-doped ZnO thin films deposited by spray pyrolysis

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Abstract. In doped ZnO (IZO), In-Al co-doped ZnO (IAZO) and In-F co-doped ZnO (IFZO) were deposited on glass substrates at 350 °C by spray pyrolysis technique. The structural, optical and electrical properties of as-deposited thin films were investigated and compared. A polycrystalline and (002) oriented wurtzite crystal structure was confirmed by X-ray patterns for all films; and the full width at half –maximum (FWHM) of (002) diffraction peak increased after co-doping. The investigation of the optical properties was performed using Uv-vis spectroscopy. The average transmittances of all the films were between 70 and 85%. Hall Effect measurements showed that the electrical conductivity of co-doped films increased as compared with IZO thin film. The highest conductivity of about 16.39 Ω⁻¹ cm⁻¹ was obtained for as-deposited IFZO thin film. In addition, the thin films were annealed at 350 °C for two hour under Ar atmosphere and their optical, electrical properties and the associated photoluminescence (PL) responses of selected films were analysed. After annealing, the electrical conductivity of all thin films was improved and the optical transmittance remained above 70%. Room temperature PL revealed that the annealed IAZO thin film had a strong green emission than that of IZO film.

1. Introduction

Transparent conducting oxides (TCOs) have attracted much attention owing to their capacity of transporting electric charge and transmitting photon in visible range. Research efforts were focused on ZnO-based transparent conducting oxides because of its low cost, high chemical stability and excellent optoelectronic properties [1]. These properties make ZnO suitable to be used as active materials in electronics and photonics [2,3]. The deposition of ZnO thin films have been reported using several techniques such as radio frequency magnetron sputtering [4], pulsed laser deposition [5], chemical vapor deposition [6], sol-gel [7] and spray pyrolysis [8,9]. Among these, spray pyrolysis has some advantages due to its easy scalability and inexpensive experimental arrangement. It is worth mentioning that the electrical properties of undoped ZnO are not enough to meet the increasing needs on fabricating high performance semiconductor devices [10]. Therefore, doping with group III elements such as In, Al and Ga presents an interesting alternative to improve their optoelectrical properties [11-13]. In addition, F doped ZnO thin films were reported to enhance the electrical conductivity by improving the mobility [14]. Thus, it is expected that co-doping with both In and Al/F element could lead to an improvement of different properties.
In this work, the co-doping effects of Al/F and In on ZnO thin films were firstly studied. Then, the effect of annealing on the optical and electrical properties was investigated. For comparative purposes, In doped ZnO thin films were prepared and their properties were also determined.

2. Experimental details
In doped ZnO (IZO), In-Al co-doped ZnO (IAZO) and In-F co-doping (IFZO) thin films were deposited on glass substrates using chemical spray technique. An homogenous solution was prepared by dissolving zinc chloride (ZnCl₂) [0.05 M] as zinc precursor and indium chloride (InCl₃), aluminum nitrate (Al(NO₃)₂), ammonium fluoride (NH₄F) as doping sources in distilled water (200ml) at room temperature. The concentration of In dopant in IZO thin film was fixed at 3 at. % and the atomic ratio of the dopant elements in IAZO and IFZO thin films were (In³⁺=3 at. %, Al³⁺=1 at. %) and (In³⁺=3 at.% , F⁻=1 at.%), respectively. The prepared solution was sprayed onto the heated substrates at a constant temperature of 350 °C. After deposition, the samples were annealed at 350 °C. Details of experimental procedure are published elsewhere [15].

The structural properties were studied by X-ray diffraction (XRD) with Cu Kα-radiation and scanning in a 2θ range from 20° to 60° by employing a Siemens D500. The optical transmittance measurements of the films were carried out in photon wavelength range of 300-800 nm using UV-Visible spectrophotometer (Perkilmer Lambda 900) and taking into account the glass in the reference beam. The electrical properties were determined at room temperature from Hall Effect equipment (ECOPIA HMS 3000) using van der Pauw’s method [16]. The photoluminescence spectra were recorded from 350 nm to 800 nm at room temperature by a 355 nm excitation line of a frequency-tripled neodymium-doped yttrium aluminum garnet (Nd-YAG) laser.

3. Results and discussion

3.1. Structural properties
The XRD patterns of IZO, IAZO and IFZO thin films were shown in figure 1. The results showed that all deposited films were polycrystalline with a structure that fit well with the ZnO wurtzite type (JCPDS no. 89-1397). In addition, no secondary phases were observed which excludes the existence of dopant based clusters. The peaks intensities were different and depended on the nature of doping element. IZO and IFZO thin films showed a high intensity of the (002) diffraction peak compared with the other peaks suggesting that the growth orientation was along the c-axis normal to the substrate. In addition, it was apparent that IAZO thin films exhibited a highly oriented (002) diffraction peak and no diffraction from randomly oriented grains can be observed indicating an improvement of stoichiometry [17].

Figure 2 showed the full width at half–maximum (FWHM) of (002) diffraction peak as a function of as-deposited films. Values of FWHM were slightly increased. The FWHM of IAZO thin films was slightly higher than those of IZO and IFZO thin film, indicating that IAZO thin films had the smallest grain size among the as-deposited films. This behavior might be caused by the stress formation as a result of the relatively high difference of ionic radius between Al³⁺ and Zn²⁺ (rAl³⁺=0.053 nm and rZn²⁺=0.074 nm) as compared with F⁻ and O²⁻ (rF⁻=0.131 nm and rO²⁻=0.138 nm) [18,19]. This is in good agreements with other reports [20-21].
3.2. Optical properties

In order to know the effect of co-doping and annealing on the optical properties of deposited thin films, the optical transmittance was measured and shown in Figure 3. All as-deposited films showed a high transmittance between 70% and 85% in the visible region and exhibited a sharp absorption edges in the wavelength region at about 375 nm.

After annealing, the optical transmittance in the visible region of IZO and IAZO decreased slightly by 4%. As indicated in the electrical properties section, annealing led to a significant increase in the carrier concentration for IZO and IAZO thin films which should be responsible for the observed decrease in these films. Similar observation was reported by You et al. who attributed this to the increase of free carrier absorption [22]. On the other hand, IFZO thin films exhibited a slight increase in transparency which might be due to an improvement of film crystallinity. Additionally, the annealed films resulted in a slight blue shift of the absorption edge. The observed variation could be explained by Burstein-Moss effect [23].

3.3. Electrical properties

Figure 4 showed the variation of the electrical parameters as a function of as-deposited samples. As it could be seen, the carrier concentration of both IAZO and IFZO thin films increased as compared with IZO thin films. Such behavior could be as a result of the substitution of F at O2- site or Al3+ at Zn2+ site which provided one free electron. It is clear that the electrical conductivity of both IAZO and IFZO thin films increased. The IFZO thin films showed the highest electrical conductivity due to its high mobility as compared with IAZO thin film, which might be due to the perturbation of the valence band by fluorine ions and therefore leaves the conduction bands free of scattering [24]. In contrast, the
lowest mobility was obtained for the as-deposited IAZO thin films. Since the carrier concentration of this thin film is in the range between $10^{19}$-$10^{20}$ cm$^{-3}$, the obtained mobility was mainly dominated by the ionized impurity scattering and grain boundary scattering [25].

The variation of conductivity and carrier concentration as a function of as-deposited and annealed thin films is shown in figure 5. The results showed that annealing led to further improvement of conductivity. The observed increase in conductivity of all thin films could be attributed to desorption of oxygen at grain boundaries, which was chemisorbed during the deposition in an oxygen containing atmosphere [26]. It worth mentioning, that the annealed IAZO thin film presented a high conductivity as compared with the annealed IFZO thin film, which could be due to the escape of volatile F from the ZnO lattice [27]. On the other hand, the most pronounced improvement in conductivity was observed for IZO thin films. The observed difference between the conductivity values of annealed IZO and IAZO films could be explained by the rearrangement of aluminum and indium ions occupying substituotional position instead of interstitial. Meanwhile, the radius of In$^{3+}$ (0.08 nm) is closer to Zn$^{2+}$ (0.074 nm) than that of Al$^{3+}$ (0.053 nm). Therefore, the substitution of Zn$^{2+}$ by Al$^{3+}$ might cause large lattice deformation which could be responsible of generating more crystal defects.

![Figure 5](image.jpg)

**Figure 5** Variation of the electrical properties of as-deposited and annealed thin films as a function of: (a) Conductivity (b) carrier concentration.

![Figure 6](image.jpg)

**Figure 6** Photoluminescence spectra of annealed IZO and IAZO Thin films.

### 3.4 Photoluminescence studies

PL study is an important method to investigate the levels of defect by analyzing the radiative recombination of the samples. Taking into account the electrical behavior of our films, IZO and IAZO annealed thin films were chosen to study their photoluminescence properties and are presented in figure 6. The intense peak at 355 nm and its second order at 710 nm were attributed to the laser source, while the peak at 381 nm corresponds to excitonic recombination corresponding to the near-band edge (NBE) emission of ZnO [28]. The second order of this peak is observed in 760 nm. A broad peak centered at about 510 nm was associated to deep level emission (DLE) and was related to the crystallinity and the lattice structural defects such as oxygen vacancies and dislocation [29].
annealed IAZO thin film showed a strong broad band of DLE which implied that the concentration of defects was very high. In contrast, the annealed IZO thin film almost passivated the oxygen based point defect and increased the NBE, indicating a good crystallinity of this film. This behavior strengthened the assumption used in the electrical properties concerning the effect of ionic radius difference.

**Conclusion**

In this work, IZO, IAZO and IFZO thin films were deposited onto glass substrates by spray pyrolysis technique, and the structural, optical and electrical properties of the samples were compared and discussed. In addition, the effect of annealing at 350 °C under Ar atmosphere on the optical and electrical properties was also investigated. All as-deposited films were polycrystalline with a (002) preferential orientation. The optical transmittance of all samples was above 70 % in the visible region. The as-deposited IFZO thin film had the highest electrical conductivity which was about 16.4 Ω⁻¹cm⁻¹. After annealing, the IAZO thin film had better conductivity than the IFZO thin film, which was around 33.3 Ω⁻¹cm⁻¹ combined with an optical transmittance above 75%. Moreover, the annealed IZO thin film exhibited the highest electrical conductivity and optical transmittance. The PL results showed that the optical qualities of IZO thin film were better than IAZO thin film, which was attributed to the lattice deformation introduced by larger ionic radius differences.

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