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Development of transparent conductive indium and fluorine co-doped ZnO thin films: Effect of F concentration and post-annealing temperature

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ABSTRACT

In the present work ZnO, In doped ZnO and In-F co-doped ZnO (IFZO) films were synthesized on heated glass substrates (350 °C) by the chemical spray technique. The effect of fluorine concentration on the structural, morphological, optical and electrical properties was studied. It was observed from X-ray diffraction (XRD) that the films have a polycrystalline structure and the intensity of the peaks depend on the doping and co-doping concentration. No diffraction peak related to dopants in XRD patterns along with shift in peaks angles to ZnO proved that In and F ions were doped into ZnO thin films. The Raman spectra confirm the hexagonal structure of the as-deposited films, and demonstrated an enhancement of the surface phonon mode of doped and co-doped films as compared to undoped films. The as-deposited films showed an average transmittance above 70%, in the wavelength range of 400–800 nm. A minimum electrical resistivity, in the order of 5.2×10^{-2} Ω cm was obtained for the IFZO thin film with 5 at.% F doping. Moreover, the electrical properties of doped and co-doped films were enhanced after post-deposition annealing. It was found that post-annealed thin films at 350 °C showed a decrease of one order of magnitude of the resistivity values. Such a transparent and conducting thin film can be suitable for optical and electrical applications owing to their low resistivity combined with high transmittance in the visible range.

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1. Introduction

Among various II–VI semiconductors, Zinc oxide (ZnO) has emerged as one of the most promising oxide materials because of its numerous potential applications in solar cells, chemical sensors and photovoltaic devices: ZnO have wide band gap of 3.2 eV and large exitonic binding energy of 60 meV at room temperature [1–3]. Many growth techniques have been introduced in order to improve the optical and electrical properties of ZnO based transparent conductive oxides (TCO) for its low cost, non-toxicity and high stability in H_2 plasma atmosphere [4]. It is well known that superior quality films are obtained by physical techniques [5–8]. However, the chemical techniques [9–10] as it the case of chemical spray technique [11], has the advantage of low cost and easy scalability, and can also be implemented to produce high quality ZnO thin films on large area. Nevertheless, the deposited film at ambient atmosphere may exhibit relatively a high resistivity [11]. Based on this assumption post-annealing treatment is an important method to reduce surface defect recombination and enhance application qualities of the deposited films.

On the other hand, until now it has been a continuous challenge to improve the electrical characteristics of the ZnO thin films which is very important for its practical application [12]. In this respect doping with the proper element, such as Al [13], Ga [14], In [15], Sn [16] and Na [17] have been studied. In addition, several researchers suggest that doping with low concentration can optimize their optical properties [18–19]. Moreover, F doped ZnO thin films show comparable electrical and optical properties to those of the group III doped films, which was attributed to it almost equal radius with oxygen ions (O^{2-} is 0.138 nm and F^{1-} is 0.131 nm) [20,21]. Therefore, the simultaneous doping of ZnO thin films with both In and F may provide double doping effects, which can be an interesting way to improve even more the electrical properties. For these reasons, several research groups focused in recent years on the effect of co-doping using fluorine and other impurities [22–25]. However, up to now, the effects of Fluorine co-doping compared to doped films have rarely been reported. For instance, Vilkumar et al. [26] have deposited In doped and In-F co-doping ZnO thin films by spray pyrolysis technique, finding that fluorine co-doping leads to an increase of resistivity as compared with In doped ZnO. However, Elfakir et al. [27] reported the deposition of doped and co-doped ZnO films with Nd and Nd-F, respectively. They reported a decrease of the resistivity value of the co-doped film with the increase of F concentration. Therefore, a complete knowledge of fluorine co-doping on the physical characteristics of ZnO thin films is far from been reached. It is worth to mention that there is no report on a detailed study of the effect of post-annealing, and F –In co-doping compared to those of In doping

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on the electrical and optical properties of chemical sprayed ZnO thin films.

In this account, spray pyrolysis technique was employed to prepare In doped and In-F co-doped ZnO at low fluorine concentration then post-annealed at argon atmosphere to study the effect of these two parameters on their physical properties.

2. Experimental details

Undoped ZnO, In doped ZnO and In-F co-doped ZnO (IFZO) thin films were deposited onto glass substrate at 350 °C by chemical spray pyrolysis. Pure zinc chloride $ZnCl_2$, indium chloride $InCl_3$ and ammonium fluoride NH_4F precursors were dissolved in 200 ml of distilled water in order to prepare the starting solution with a concentration of 0.05 M. For preparing doped and co-doped thin films, the In concentration was fixed at 3 at.% while the F concentration was varied from 0, 1 and 5 at.%, IZO, IFZO1 and IFZO5 respectively. Spray rate was held constant at 2.6 ml/min. The as-deposited doped and co-doped films with the lowest resistivity were subjected to post-annealing in Ar gas inside a tubular furnace for 2 h at 350 °C and 400 °C. The detailed description of the experimental procedure has been given elsewhere [11].

The as-deposited thin films were characterized to evaluate their physical properties. The crystal structural and morphological studies were investigated by the X-ray diffractometer ($\lambda = 1.5405$ Å, Siemens D500) with CuK_α in the Bragg angle ranging between 20 and 60° and Scanning Electron Microscopy (SEM, FEI Quanta 200, operating voltage is 30 kV), respectively.

The grain size is simply determined using the Scherrer formula [28]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where λ, θ and β are X-ray wavelength, the Bragg's diffraction angle and the full width at half maxima of the peak corresponding to "θ" value, respectively.

Quantitative information concerning the preferential crystallite orientation along the [002] direction is obtained from the analysis of the different texture coefficient (TC) (hkl) associated to the texture of a particular plane. Its deviation from unity indicates a stronger preferred growth along the [hkl] direction. TC is defined as [29]:

$$TC = \frac{I(hkl)/I_0(hkl)}{n^{-1}\sum_{i=1}^{i=n} I(hkl)/I_0(hkl)} \tag{2}$$

where $I(hkl)$ indicates the X-ray diffraction (XRD) intensity obtained from the film, 'n' is the number of diffraction peak considered and $I_0(hkl)$ is the intensity of the reference diffraction patterns (JCPDS data card 01–1136).

The lattice constants a and c were calculated by using the following equation [30]:

$$\frac{1}{d^2(hkl)} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \tag{3}$$

where (hkl) is the Miller indices of the planes and d(hkl) is the inter-plane distance.

The optical transmittance spectra were obtained using UV–Visible spectrophotometer (PerkinElmer Lambda 900), and taking into account the glass in the reference beam. Additionally, Raman spectra were carried out at room temperature in the backscattering geometry by means of the Horiba's LabRam ARAMIS spectrometer equipped with a multichannel CCD detection system. The incident laser light with the wavelength of 325 nm was used. Finally, the electrical resistivity, the carrier concentration and the mobility were measured at room temperature by an ECOPIA Hall Effect instrument.

3. Results and discussion

3.1. Structural characterization

Fig.1 exhibits the XRD patterns of undoped ZnO, IZO and IFZO thin films deposited with different F contents. All diffraction peaks can be indexed into the ZnO hexagonal wurtzite structure, indicating that In and F ions did not change the structure of ZnO. The absence of In_2O_3 or other impurities peak excludes the existence of F or In-based clusters within the detection limit. This finding indicated that F^- and In^{3+} ions were incorporated into the ZnO lattice and that In and F co-doping didn't alter the hexagonal wurtzite structure of the films. All the films show a strong (002) peak compared with the relative weak peaks of the (100), (101), (102) and (110), suggesting that they have a c-axis preferred orientation. On the other hand, the doped and co-doped thin films showed higher intensity of the (101) peak than that of the undoped film and in parallel enhanced feature of the (102) peak. The same behavior was seen after single doping of ZnO by In and F [15,31]. It is found that co-doping not only increases the intensity of the (101) peak, but also induces the evolvement of new diffraction peak (110) that is otherwise absent in the undoped and doped films, however, it remains lower than the others.

From Table 1, it can be seen that all the films exhibited a high TC values for the (002) plane, indicating that all the thin films had a c-axis preferred orientation. The average grain size, inter-plane distance and lattice constants α and c obtained from the XRD data for undoped ZnO, IZO and IFZO films are presented in Table 1. Compared with undoped ZnO, the grain size of IZO and IFZO thin films became small, indicating that doping and co-doping reduce the crystal quality. Similar behavior has been reported by other authors on the deterioration of single doped ZnO films with F and In [31–33]. The lattice parameters increased for IZO film then decreased for IFZO films as compared with the doped film. This could be ascribed to the bigger ionic radius of the In^{3+} (0.080 nm) as compared to Zn^{2+} ions (0.074 nm) and the smaller ionic radius of F^- ions (0.131 nm) replacing O^{2-} ions (0.138 nm). Moreover, increasing or decreasing in lattice parameters can be related to the residual stress in the film [34].

SEM images of the as-deposited films under different doping concentration are shown in Fig. 2. It is apparent that the surface morphology was strongly modified by doping and co-doping. For undoped ZnO, the particles were observed to have a rounded shape, similar size of about 300 nm and are uniformly distributed over the surface. The surface morphology of IZO consists of many tetrahedral-shape particles with different sizes (350–500 nm). Similar microstructure is observed in IFZO1 films with relatively larger particles (600–800 nm) that appeared among the smallest which lead to rougher surface. As F doping

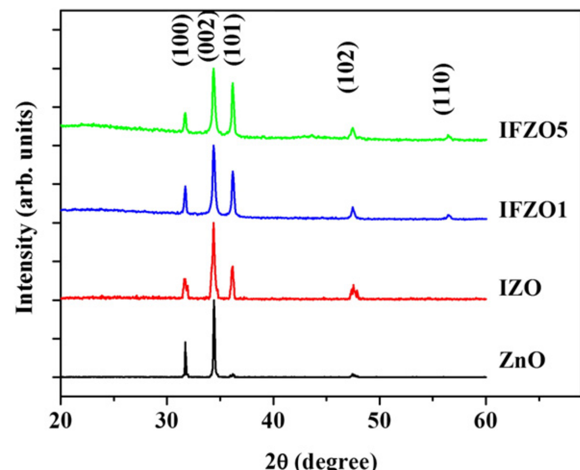

Fig. 1. XRD patterns of ZnO, IZO and IFZO thin films.

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