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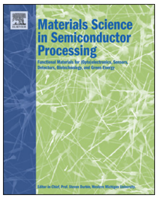

Study of defects in Li-doped ZnO thin films

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ABSTRACT

Li-doped ZnO films were deposited on glass substrate by sol-gel spin coating technique. In order to investigate the effect of Li doping on ZnO thin films properties, we have varied the Li doping ratio in the range of 0–10%. The structural and optical properties of samples have been investigated by X-ray diffraction and UV–Vis spectroscopy. XRD analysis reveals that doped and undoped films have an hexagonal Wurtzite structure. The optical measurements indicate that Li doping causes the red shift of the absorption edge. Films photoluminescence spectra do not contain any defects peak related to Li atoms. Being too close to the valence band, the Li defect level is buried in the band tail width states; this explains the difficulty of its detection. However, the effect of Li doping, manifests through its oxygen vacancy defects promotion to the detriment of oxygen interstitial oxygen defect.

1. Introduction

Zinc oxide thin films have attracted an increasing interest due to their excellent semiconducting properties [1–3]: a direct wide band gap of 3.37 eV and large excitation binding energy (60 meV) at room temperature [4]. ZnO has received a considerable attention as a promising material for electronics, optics and optoelectronics devices fabrication. Some of these applications involve the photoluminescence and electroluminescence properties of ZnO. Therefore, a large number of investigations have been devoted to the study of ZnO photoluminescence [5]. The visible emission of ZnO is close related to the intrinsic defects such as oxygen vacancies, zinc vacancies or oxygen interstitial and doping atoms. Several emissions in ZnO have been observed green [6], red-orange [7] and yellow [8].

Doping ZnO with atom causing the formation of shallow level is among routes to enhance the optical emission of ZnO [9]. Therefore, an effort devoted to ZnO doping has been carried out [10–12]. Introducing extrinsic doping atoms can alter the emission wavelength spectra of ZnO films. Therefore, several impurity atoms effect has been investigated such as Li, Al [13,14], Mg [15] and Eu [16]. Beside the extrinsic defects, the effect of native ones on the photoluminescence properties of ZnO structures has been extensively studied in the literature [17–19].

The most promising doping atoms for p-type ZnO production are the I and V elements group, while, theory suggests some difficulties in achieving shallow acceptor level [20]. Therefore, Li doping of ZnO to produce p type is still controversial. Recently, Ardyanian et al. [21] indicated that the formation of deep acceptor levels implies not to contribute significantly to p-type conduction. Despite that ZnO photoluminescence is extensively studied, Li doping effect on the ZnO photoluminescence is less investigated. Introduction of doping atoms in the semiconductor network is usually accompanied by the creation of defect levels within the material band gap. The present study aims the investigation of the defects related to Li doping atoms using photoluminescence technique.

In the present work, we have prepared Li-doped ZnO thin films with different Li doping ratio by sol-gel technique. The effect of Li doping ratio on ZnO films structural, optical and photoluminescence properties are investigated.

2. Experimental details

2.1. Synthesis of pure and Li-doped ZnO thin films

Sol-gel spin coating technique was utilized to prepare Li-doped ZnO thin films. The solution was prepared using zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) as Zn precursor, lithium-chloride ($LiCl_3$) as a dopant source, mono-ethanolamine (MEA, $C_2H_7N_{14}$) as a stabilizer and 2-methoxyethanol as a solvent. The molar ratio of MEA to zinc acetate was fixed to 1 and the concentration of lithium-chloride was varied from 2 to 10 at%. The solution was stirred at 60 °C for 2 h before aged at room temperature for 24 h to yield clear and homogeneous solution.

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The solution was then used for the deposition process by spin-coating technique. The used substrates were microscope glass. The spin coating was performed at room temperature using 10 drops of solution per deposition with a speed of 2000 rpm for 30 s and 3000 rpm for 10 s. After the deposition process, the thin films were preheated in atmosphere ambient at 300 °C for 10 min to evaporate the solvent. After repeating the coating procedure 7 times, the films were annealed at 500 °C for 1 h in air ambient using a hot plate.

Sample code are named as L0ZO, L2ZO, L3ZO, L4ZO, L5ZO and L10ZO, according the nominal Li loading of each sample.

2.2. Characterizations

The crystalline phases of the obtained thin films were identified by X-ray diffraction (XRD) using a Bruker D5005 powder X-ray diffractometer using a CoKα source (1.78901 Å radiation). The average crystallite size (G, in Å) was estimated from the Scherer's equation [22]:

$$G = \frac{0.9\lambda}{B\cos\theta_B} \tag{1}$$

where λ is the X-ray wavelength (1.78901 Å), θ_B is the maximum of the Bragg diffraction peak (in radians) and B is the line width at half maximum.

The optical transmittance of the powders was determined using a Schimadzu UV-3101 PC spectrophotometer with integrating sphere in the wavelength range 200–900 nm.

PL measurements were performed under excitation of the 325 nm HeCd laser line.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD diffraction patterns of undoped and Li doped ZnO thin films. As can be deduced from these patterns, films have a hexagonal Wurtzite structure with a strong orientation along the (002) plan. Regardless the deposition technique, this preferential orientation have been reported by several authors working on ZnO. This is due to the fact that the plan (002) requires less energy to be formed [23].

In Fig. 2 we have reported the variation of (002) peak intensity and position in the same plot. At low doping range from 0% to 3%, the peak intensity increases with Li concentration, this is consistent with crystallite size increase as shown in Fig. 3. This can be attributed to the modification of the nanocrystalline growth as suggested by Chu et al. [24]. It is well known, in thin film growth process, that any foreign atom such as doping atom acts as a new nucleation center; this may explain the increase in the peak intensity and crystallite size with increasing the doping ratio until 3%. However, above 3%, due to more Li atoms incorporation in ZnO network, further increase in the nucleation center hinders the continuous crystallite growth [25]. Consequently, the crystallite size enlargement is stopped due to the completion between adjacent growing nanocrystals. This is consistent with the reduction of both peak intensity (Fig. 2) crystallite size as a function of Li doping (Fig. 3). According to these results, 3% doping level seems to be a critical one, where Li atoms start altering the host network beyond this ratio.

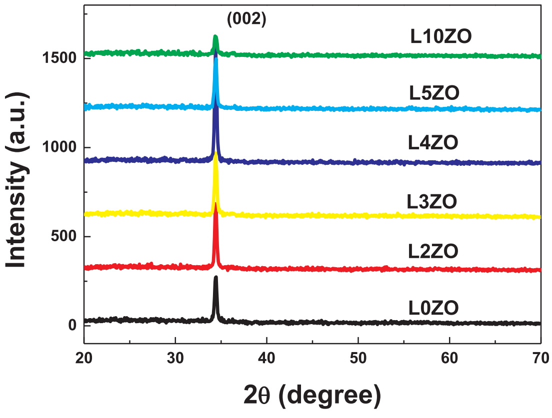

Fig. 1. X-ray diffraction patterns of pure and Li doped ZnO thin films.

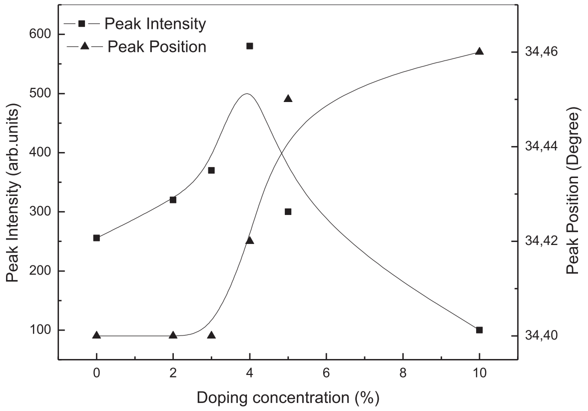

Fig. 2. Variation of the intensity and the position of the diffraction peak (002).

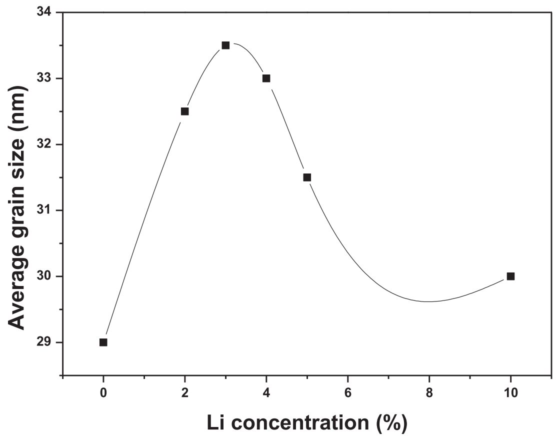

Fig. 3. Variation of average crystallite size as a function of Li concentration.

As shown in Fig. 2, the (002) peak position remains unchanged at low doping ratio (less than 3%), while above this ratio, the peak slightly shifts gradually towards higher angles with increasing the doping ratio. The peak shift has been reported by several authors working on Li doped ZnO [21,26,27]. The shift towards higher angle can be attributed to stress increase with Li incorporation in film network as suggested by [26]. However, Ardyanian et al. [21] has reported an alternating shift to higher and lower angles, they implement this behavior to the completion between tensile and compressive stress in the lattice, due to the Li substitution at the interstitial and Zn sites respectively. In our case the observed shift towards the higher angles, as shown in Fig. 2, suggests that Li is mainly incorporated in the interstitial sites.

In Fig. 4 we have regrouped the transmittance spectra of different Li doped ZnO thin films. All films exhibit a large transmittance in the visible range, mostly in the order of 90%. As can be seen, Li doping do not alter the transmittance level in the thin films.

The optical band gap is estimated by using Tauc plot [28]. It is based on the determination of the intercept of the linear extrapolation of $(\alpha h\nu)^2$ as a function of photon energy plot with the X- axis. The variation of the optical band gap as a function of Li doping is reported in Fig. 5. In general, Li doping causes the optical gap shrinking. It varies from 3.3 eV in the undoped film to 3.27 eV in 3% Li doped one. Salah