

P-type transparent conducting Li-doped ZnO thin films prepared by ultrasonic spray pyrolysis method

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Abstract—Li-doped p-type ZnO (ZnO :Li) thin films have been prepared under atmospheric pressure by ultrasonic spray pyrolysis method (USP) at optimized substrate temperature of 350 °C. 0.3 M solution of zinc acetate in a mixture of Methanol was employed. Dopant source was lithium chloride (LiCl) and the molar ratio of Li/Zn is 1%. The results show that Li-doped ZnO thin films were transparent, uniform and strongly adherent to the substrates. The optical transmittance was about 85% in a visible range. The optical band gaps of the films were calculated from Tauc plot. The Raman spectrum shows dominant peaks around 437cm⁻¹, corresponding to the E₂(high) mode of the Raman active mode, a characteristic peak for the wurtzite hexagonal phase of ZnO. No secondary phases were observed for the simple synthesis process adapted in the present work for the Li-doped ZnO films. The p-n hetero-junction were prepared by depositing the Li-Doped ZnO film on the n-type silicon substrate. The current-voltage characteristics exhibited the rectifying behavior of a typical p-n junction. Such hetero-structures are promising to find potential applications in electronic and optoelectronic devices.

Keywords: Ultrasonic spray pyrolysis; ZnO:Li; optical band gap

I. INTRODUCTION

ZnO with a direct band gap of 3.37 eV and large exciton binding energy of 60meV has attracted considerable attention in the last decade due to its potential optoelectronic applications [1,2]. To fabricate light-emitting devices, an important issue is the preparing of high quality p-type ZnO films. However, it had been proven difficult due to the self-compensation effect [3], deep acceptor level and low solubility of acceptor dopant [4–6]. In recent years, considerable efforts had been made to create p-type ZnO using group-V elements such as N, P, as and Sb [7–10]. Unfortunately their acceptor levels are theoretically identified to be deep with low solubility limits. In contrast to that, group-I species substituting for Zn theoretically possess shallow acceptor levels [11,12]. Furthermore Li

element is the best candidate in producing p-type ZnO in regard to strain effects and energy levels of substitutional Li_{Zn}. Many techniques such as pulsed laser deposition (PLD) [13], metalorganic vapor phase epitaxy (MOVPE) [14], magnetron sputtering [15], chemical vapor deposition (CVD) [16,17], sol-gel [18], and spray pyrolysis [20–22,23] have been used to deposit ZnO films. Among these techniques, spray pyrolysis has been proved to be a simple and inexpensive method, particularly useful for large area applications. Furthermore, ZnO films can be grown at atmospheric pressure by the spray pyrolysis technique, resulting in less intrinsic defects such as oxygen vacancies than in films deposited in a high vacuum environment. Therefore, the spray pyrolysis technique is favorable for weakening the compensation effect by intrinsic defects and realizing p-type doping. On that supposition, low-resistivity p-type conduction has been achieved in N-In(Al) co-doped ZnO films deposited by the ultrasonic spray pyrolysis (USP) techniques [19–21]. However, the co-doping method could incorporate excessive impurities that would be harmful for the electrical and optical properties of ZnO films and devices. In this work, Li-monodoped ZnO thin films and p-ZnO/n-Si hetero-structure were prepared by the ultrasonic spray pyrolysis (USP) technique. The electrical and optical properties of Li-doped ZnO thin films were studied and p-type behavior was investigated in detail.

II. EXPERIMENTAL DETAILS

ZnO:Li films were co-deposited onto (100) oriented n-type Si and glass substrates for the different specific characterizations by ultrasonic spray pyrolysis technique under atmospheric pressure. The starting solution was 0.3M of zinc acetate (Zn(CH₃COO)₂·2H₂O) prepared by dissolving the equivalent mass of zinc acetate in methanol. Methanol is obvious choice because of its volatility and thus facilitating quick transformation of the precursor mist into

vapor form. A few drops of acetic acid were added to stabilize the solution and prevent precipitation of zinc hydroxide. The acidity of the spray solution was pH = 5. The compound source of doping was lithium chloride (LiCl₄). The percentages of doping the starting solution are [Li/Zn]=5 at%, and substrate temperature was fixed at 350°C. The deposition time was fixed for 1 hour. The obtained mixture was stirred at 60°C for 2 hours to yield a clear and homogenous solution. The spray rate was maintained at 0.25 L/min. The thickness of undoped and Li-doped ZnO films, is approximately equal to 650 nm and was measured by a Dektak III stylus profilometer (Sloan technology). The Raman spectra are recorded using a Jobin Yvon T6400 micro-Raman spectrometer equipped with an Ar + laser (514.5 nm) excitation and with a low power of about 40 mW, in order to avoid any beam-induced crystallization during measurements. Optical transmittance and reflectance spectra at room temperature of the films have been recorded in the wavelength range of 280-2000 nm using a double beam UV-VIS-NIR 5E Varian spectrophotometer. FTIR absorption was measured over the frequency range 400-4000 cm⁻¹ and with a resolution of 4 cm⁻¹, using a Bruker Vector 33 Fourier transform infrared (FTIR) spectrometer. Electrical properties were measured by picoammeter (KEITHLEY 617).

III. RESULTS AND DISCUSSION

A. Optical results:

Fig.1 shows the optical transmittance curves at wavelength from 280 to 2000 nm for ZnO and Li doped ZnO films deposited on glass substrates. It is evident that the films exhibit high transparency in both visible. The average transmittance is greater than 90% in the visible region and a reflectance of about 2%, indicating the good quality of the deposited films with low scattering or absorption losses. Due to the fundamental absorption in the vicinity of the band gap, the transmittance in the ZnO and ZnO:Li films decreases sharply as the wavelength reaches the ultraviolet range caused by scattering from defects.

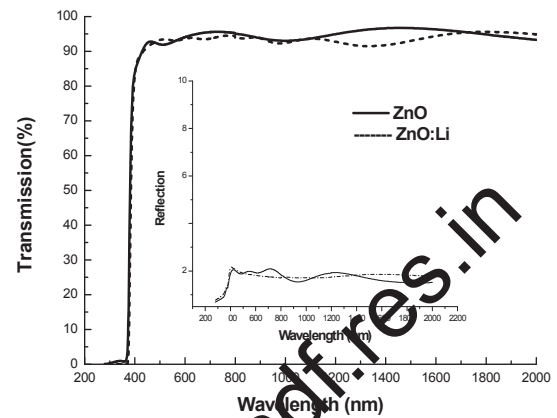


Figure 1. Transmittance spectra of the undoped and Li-doped ZnO films deposited at 350 °C. (The inset shows reflectance spectra of ZnO and Li-doped ZnO films.)

The optical band gap E_g can be determined from the absorption coefficient α calculated as a function of incident photon energy $h\nu$. Near the absorption edge region, the absorption spectra $\alpha(h\nu)$ of the films have been obtained from the optical transmission and reflection measurements at 300 K. The absorption coefficient is obtained from the following equation [23]:

$$\alpha = \frac{1}{d} \ln \left(\frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2} \right) \tag{1}$$

where α is the absorption coefficient, d is the thickness of the film, R and T are the reflectance and the transmittance respectively. For a direct gap semiconductor such as ZnO the absorption coefficient has the following spectral dependence [24]:

$$\alpha(h\nu) = A(h\nu - E_g)^{\frac{1}{2}} \tag{2}$$

Where A is a constant, $h\nu$ is the photon energy and E_g is the optical band. Fig. 2 shows plots of $(\alpha h\nu)^2$ versus $h\nu$ where the optical band gaps of the films were calculated from these plots.

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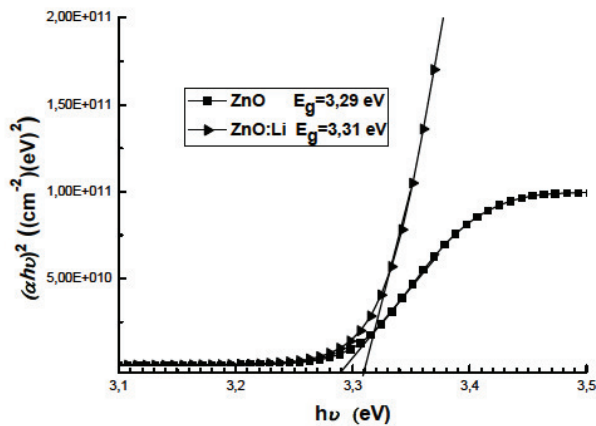


Figure 2. Plots of $(\alpha h\nu)^2$ versus $h\nu$ for undoped and Li-doped ZnO deposited at 350 °C.

It is clear that the admixture of ZnO with Li ions generally increases the value of E_g over that of pure ZnO films (from 3.29 eV for ZnO to 3.31 eV for Li-doped ZnO). We can say that Li doping converts the shallow donor Zn sublevels to deep sublevels below the conduction band. This coincides with the results of Sbrveglieri et al. [25]. They conclude that Li ions lead to the formation of two deep level donors in ZnO thin films which are, respectively, 0.38 and 0.81 eV below the conduction band, while the undoped films show two levels at 0.16 and 0.48 eV.

B. FTIR Results:

FTIR spectra of pure and Li-doped ZnO thin films are shown in Fig. 3. A series of absorption peaks from 1000 to 4000 cm^{-1} can be found, corresponding to the carboxylate and hydroxyl impurities in materials. To be more specific, a broad peak in the range 3200–3600 cm^{-1} is due to OH stretching mode of hydroxyl group. Peaks around 2900 cm^{-1} are due to C–H (acetate) stretching vibration of alkane groups. The two principal absorption peaks are observed between 1400 and 1650 cm^{-1} , corresponding to the symmetric and asymmetric stretching of the carboxyl group (C=O). The band in the range of 400–550 cm^{-1} is due to the Zn–O and Zn–Li–O stretching mode. There is no evidence of O–H stretching at 2550 cm^{-1} and O–H around 1650–1750 cm^{-1} , suggesting that no moisture was adsorbed in the samples. The deformation band of C=O at around 1000 cm^{-1} , and absorption peaks observed ordinary between 2300 and 2400 cm^{-1} due to adsorbed CO₂ molecules in air are absent in our FTIR spectra indicating the good quality of our films. FTIR spectra of pure and Li-doped ZnO films of the present investigation are in good agreement with the reported values [26,27].

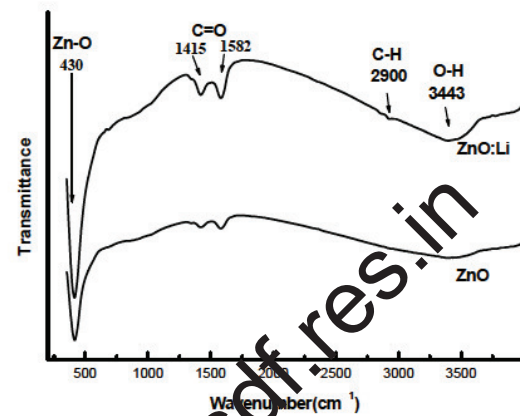


Figure 3. FTIR spectra of undoped ZnO and Li-doped ZnO: 1at%.

C. Raman results:

In order to investigate the effects of substrate on ZnO:Ag films further the Raman spectra of the film was measured. It is known that Raman scattering is considered to be the most powerful nondestructive technique to study the crystal quality, structural disorder, and defects in the doped semiconductor alloy. It gives important information about the local structural changes due to incorporation of highly mismatched Li⁺ ions into the ZnO lattice. The ZnO is wurtzite structure with C_{6v}-4(P63mc) point group symmetry having six Raman active optical phonon modes at the center of the Brillouin zone [28]. The frequencies of the fundamental optical modes in ZnO are $E_2(\text{low}) = 101 \text{ cm}^{-1}$, $E_2(\text{high}) = 437 \text{ cm}^{-1}$, $A_1(\text{TO}) = 380 \text{ cm}^{-1}$, $A_1(\text{LO}) = 574 \text{ cm}^{-1}$, $E_1(\text{TO}) = 407 \text{ cm}^{-1}$, and $E_1(\text{LO}) = 583 \text{ cm}^{-1}$.

The unpolar E_2 modes have two frequencies, namely, $E_2(\text{low})$ and $E_2(\text{high})$ corresponding to the Zn and O sublattice vibrations. The A_1 and E_1 modes are polar and hence, exhibit different frequencies for the transverse-optical and longitudinal-optical (LO) phonons, because of the macroscopic electric field associated with the LO phonons. The different scattering geometries allow different vibrational modes in the Raman spectra. Moreover, changes in the lattice spacing and chemical environment may shift the vibrational frequencies. Fig. 4 shows the Raman spectra of the ZnO:Li films deposited on n-Si substrate.

The peak at 522 cm^{-1} (marked by P) is due to scattering from silicon substrate. The characteristic 436 cm^{-1} peak, assigned to the non-polar E_2 optical phonon mode, is present for the pure and Li-doped ZnO thin films, with a similar shape.

As can be seen in the figure, the Raman spectrum of ZnO:Li differs very little from the corresponding spectrum of pure ZnO. Small shift in Raman spectra towards higher wave number indicate the strain in the ZLO and multilayer thin film due to Li incorporation. No Raman peak of Li₂O

appeared in the spectra of the ZLO, indicating the absence of secondary phases in Li doped samples, which are important to determine the optical and electrical properties of the film and hence for the application in optoelectronic devices.

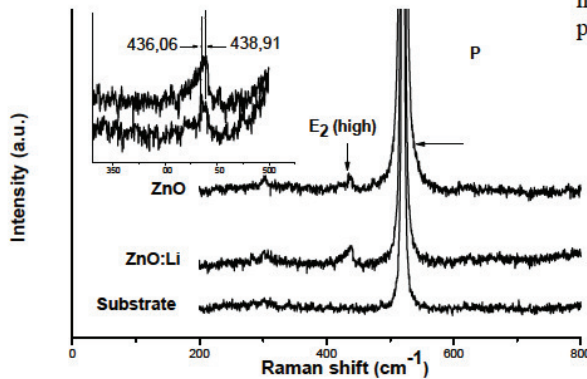


Figure 4. Raman spectra of ZnO and ZnO:Li along with Raman spectra of Si substrate for reference (The inset shows the shift of E₂ high mode).

D. P-N hetero-junction:

To confirm the p-type conductivity of ZnO :Li films ,a layer of 6000 to 6500Å of Li-doped ZnO (Li/Zn=1%) was deposited on n-type silicon <100> substrate at 350°C , as shows in fig 5.

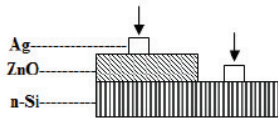


Figure 5. Illustration of a p-ZnO:Li/n-Si hetero-junction which had silver (Ag) electrodes.

The measurement of I-V characteristic was accomplished through use of the four point technique at room temperature. The Ohmic behavior is confirmed by the completely linear I-V curves for the Ag contacts on the both n-Si substrate and ZnO thin films, as shown in the inset of Fig 6 . The I-V characteristics of the ZnO:Li/n-Si hetero-junction are shown in Fig 6. It exhibits apparently electrical rectification behavior of a typical p-n junction, although there is similarities to some extent as compared with an ideal p-n junction. For a clear interpretation, electrons from the n region near the p-n interface tend to diffuse into the p region. As electrons diffuse, they leave positively charged ions (donors) in the n region. Likewise, holes from the p-type region near the p-n interface begin to diffuse into the

n-type region, leaving fixed ions (acceptors) with negative charge.

The formation of p-n hetero-junctions firmly confirms the p-type conductivity of ZnO:Li 1% films. The realization of p-type ZnO film may be due to the existent of Li acceptor that Li atoms substitute for Zn atoms acting as effective acceptor in ZnO [29]. The p-type ZnO thin film fabricated here are still in the early stages in their development process.

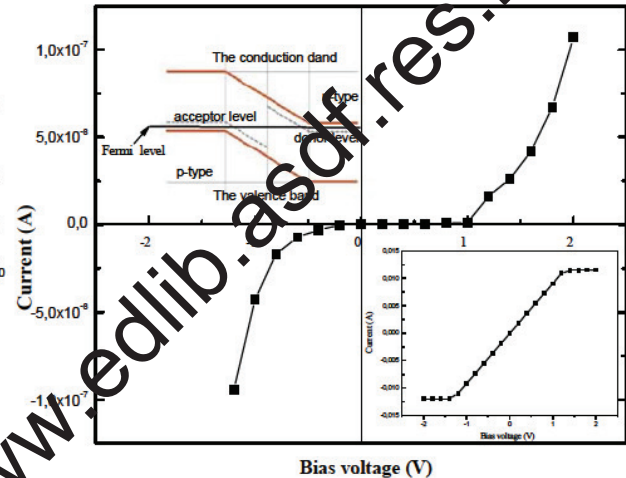


Figure 6. The Current-voltage curves of p-ZnO:Li/n-Si hetero-structures and inset shows the I-V characteristics of Ag contacts.

VI. CONCLUSION

The undoped and Li-doped ZnO 1%at films growth by ultrasonic spray pyrolysis method under atmospheric pressure were investigated systematically. All films have an average transmittance greater than 85% in the visible region and a reflectance of about 2%. The optical band gaps increased from from 3.29eV for ZnO to 3.31eV for Li-doped ZnO. FTIR analysis confirms the formation of ZnO. absorption peaks observed ordinary between 2300 and 2400 cm⁻¹ due to adsorbed CO₂ molecules in air are absent in our FTIR spectra indicating the good quality of our films. the Raman spectra shows that the structure is hexagonal wurtzite by the presence of the peak around 436 cm⁻¹. The formation of p-n hetero-junctions firmly confirms the p-type conductivity of ZnO:Li films. The p-n hetero-junctions (hetero-structure) fabricated here are still in the early stages in their development process. There is still room for optimization in both the growth and processing conditions for the p-n junction quality.

The Li mono-doping method may have its great potential in fabricating good p-type ZnO for practical applications.

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