



# Structural, optical and electrical properties of Sn–N codoped p type ZnO thin films prepared by spray pyrolysis technique for diode applications



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## ABSTRACT

The efficacy of tin-nitrogen codoping (Sn–N) in ZnO thin films deposited on glass substrates by spray pyrolysis technique to achieve a p type transparent conductive material is investigated. Monodoping ZnO with N altered the conductivity type but the resistivity is too high making it practically impossible to be useful in optoelectronic applications. But Sn–N codoping increased the hole concentration and obtained comparatively low resistivity because codoping enhanced the acceptor incorporation by forming acceptor-donor-acceptor complex in the band gap. The XRD analysis revealed the dependence of dopant incorporation on the texture and microstructure of the ZnO thin films. Further, the optical energy gap of N doped film decreased compared to undoped one due to the merging of impurity bands with the valence band while higher energy gap value for codoped film which might be due to the Burstein-Moss effect arising from increase in carrier concentration and also due to degraded crystallinity.

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## 1. Introduction

In the present scenario, zinc oxide (ZnO) thin films achieved the attention of materials researchers because of its unique properties such as large energy gap ( $\sim 3.37$  eV), large free exciton binding energy ( $\sim 60$  meV), piezoelectric properties, etc. Moreover, we can tune its electrical conductivity from insulating via semiconducting to conducting by adding suitable impurities and also it is possible to tailor the energy gap of ZnO by making alloys with materials having different band gap like MgO, CdO, etc. In addition it is a low-cost, easily available, less-toxic and biocompatible material. So ZnO is a prominent transparent conducting oxide material in a variety of potential device applications such as solar cells [1], optical waveguides [2], light emitting diodes [3], thin film transistors [4], gas sensors [5], etc. The field of electronics is mainly based on developing functional p–n junctions. Developing junctions solely based on one kind of material is a challenge for material scientists. Thus in order to open up the field of 'Transparent Electronics', we have to develop p type ZnO. Efficient exciton emission can persist in ZnO even at room temperature due to the large free exciton binding energy. Hence the oscillator strength of excitons in ZnO is typically much larger than that of direct electron-hole transitions compared to other direct band gap semiconductors. This makes ZnO a promising material for optical devices that are based on excitonic effects. Thus if it becomes viable to develop p type

ZnO thin film, it will be more easy to fabricate monolithic ZnO light emitting diodes (LEDs), laser diodes (LDs) and photodetectors.

ZnO is intrinsically n type semiconductor due to the presence of zinc interstitials or oxygen vacancies and is not amenable to both types of doping. Even though group V and group I elements can be used as acceptors in ZnO, it is harder to develop a p type counterpart to ZnO. This is mainly due to problems such as its self compensating effect, deep acceptor levels and low solubility of acceptor dopants [6]. ZnO has asymmetric doping limitations and strongly favours n type doping. This asymmetry in its ability to be doped n type or p type is called 'unipolarity' [7]. The main contribution to the binding energy of the ionic compounds favouring wurtzite structure is electrostatic in nature and is called the Madelung energy. While n type doping using donors causes a decrease in Madelung energy, acceptor doping gives rise to increase in Madelung energy and hence unstable ionic charge distributions within the p type doped crystals. The method of codoping of group III and group V elements can be utilized to improve the acceptor solubility and thereby making acceptor levels shallower [7]. It should be important here that the donor dopant is not the p type killer, but the reactive codopant which activates acceptors. A few reports are available in the literature studying the feasibility of Al–N codoping [8], In–N codoping [9–11], B–N codoping [12], Ga–N codoping [13], Ag–N codoping [14], etc. in order to improve the p type electrical performance of ZnO thin films. So in this study we tried to develop a p type ZnO thin film codoped with Sn (a group IV element) and N as a step to realize ZnO homojunction diodes.

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Numerous techniques have been employed in depositing ZnO thin films like atomic layer deposition (ALD) [15], chemical vapour deposition (CVD) [16], pulsed laser deposition (PLD) [17], spray pyrolysis [18], sputtering [19], sol-gel technique [20,21], etc. Among these, spray pyrolysis has many advantages like simplicity, low-cost, possibility of mass production, no need of vacuum at any stage, etc. In the present work, we studied the effect of tin-nitrogen (Sn–N) codoping on the structural, morphological, optical and electrical properties of ZnO thin films deposited on glass substrates by spray pyrolysis technique to be useful in the field of optoelectronics.

## 2. Materials and methods

Thin films of undoped ZnO, nitrogen (N) doped ZnO and tin-nitrogen (Sn–N) codoped ZnO with 2 at.% Sn were deposited on pre-cleaned glass substrates by spray pyrolysis (Holmarc Spray Pyrolysis Equipment Model No: HO-TH-04) technique. Throughout the experiment, the concentration of the precursor solution was kept fixed at 0.4 M. The starting solution was prepared by dissolving equivalent mass of zinc acetate dihydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] in a mixture of methanol, deionised water and acetic acid taken in the ratio 65:30:5 (The concentration and composition of the precursor solution were previously optimized). The role of acetic acid in the precursor solution is to stabilize the solution and to prevent the precipitation of zinc hydroxide, thereby improving the optical quality of the films. Also in spray pyrolysis technique, we can easily accomplish doping during the preparation of precursor solution by simply adding the salt containing the desired dopant. In this study, ammonium acetate [ $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ], due to its high solubility in water and low melting temperature, was chosen as the source of nitrogen. The precursor solution for ZnO:N thin films with Zn:N = 1:2 was prepared by adding the required quantity of ammonium acetate in the previous solution. In order to study the effect of codoping, desired quantity of stannous chloride [ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ] – the source of Sn – were added to the precursor solution of ZnO:N by taking the Sn/Zn ratio as 2 at.%. The resulting solutions were then sprayed over pre-cleaned glass substrates which were kept on a hot plate maintained at  $400 \pm 10^\circ\text{C}$  to obtain three series of thin films. In order to be more authentic, we prepared four different samples of each kind under the same preparative conditions.

The structural characterization of the films were carried out by using Rigaku Miniflex 600 X-ray Diffractometer with  $\text{CuK}_\alpha$  radiation of wavelength,  $\lambda = 1.5406 \text{ \AA}$ . The composition analysis of the samples was done by Energy Dispersive X-ray spectroscopy (EDX) on JEOL Model JSM – 6390 scanning electron microscope attached with JEOL Model JED – 2300 operated at 20 keV. The morphological studies were also performed on the same scanning electron microscope (SEM). The optical transmission spectra of the thin films were obtained in the 300–900 nm spectral range using Jasco V-650 double beam spectrophotometer. The electrical properties were measured by the Van der Pauw method using the Hall measurement system (Ecopia Hall Effect Measurement System) with a magnetic field strength of 0.550T at room temperature and carried out six trials for each and every film. Thickness of the deposited

samples was determined by gravimetric method using Shimadzu AY 220 Model Balance and the values were presented in Table 1.

## 3. Results and discussions

### 3.1. Structural properties

Fig. 1 shows the XRD pattern of the spray pyrolysed thin films of undoped ZnO, N doped ZnO and Sn–N codoped ZnO. All the films exhibited polycrystalline nature with hexagonal wurtzite structure and there was no phase other than ZnO (JCPDS Card No. 36-1451). This indicates that Sn and N were successfully incorporated in the lattice without disturbing the ZnO structure. For the undoped ZnO thin film, (1 0 0), (1 0 1), (1 1 0) and (1 1 2) reflection peaks appeared predominantly with a preferential orientation along the (1 0 0) plane. With N doping, reflected intensity at (1 0 1), (1 1 0) and (1 1 2) planes decreased and a reflection peak corresponding to (0 0 2) plane appeared. The peaks at (1 0 0), (1 1 0) and (1 1 2) planes completely disappeared and new peaks appeared at (1 0 2) and (1 0 3) planes for Sn–N codoped ZnO film. Also the film showed preferential orientation along the (0 0 2) plane indicating that most of the grains have strong c-axis orientation normal to the substrate surface. Thus doping plays a vital role in orienting crystal planes and consequently modifies the microstructure. The change in the preferential orientation of the doped films is related to the nucleation process and to the difference in surface reactions. The crystal growth of ZnO surfaces and hence the final shapes of the crystals are believed to be related with the various physical and chemical interactions of ad-atoms and the film. In the case of doping, there will be a change of physical and chemical interactions between the ad-atoms and the film during film formation and consequently a change in energy adsorption [22]. Since the surface affinity for different dopants to each orientation is different, the growth rate along different facets can be quite different. This may be the reason for the drastic change in preferential orientation of the codoped films. Many others reported similar results upon doping [23–26].

Average crystallite size of the prepared samples for the most intense diffraction peak was calculated using the Scherrer formula [27]

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where 0.9 is the value of the shape factor,  $\lambda$  (=1.5406 Å) is the wavelength of the X-rays used,  $\beta$  is the full-width at half maximum intensity in radians and  $\theta$  is the Bragg's angle.

The defects in the films can be quantified by computing the dislocation density ( $\delta$ ) which is defined as the length of dislocation lines per unit volume of the crystal [28]. For preferential orientation it was calculated using the formula given below [29]:

$$\delta = \frac{1}{D^2} \quad (2)$$

The calculated values of average crystallite size and dislocation density were presented in Table 1. It was clear that all the films were nano-structured and doping resulted in decrease in average

**Table 1**  
Structural parameters including average crystallite size (D), dislocation density ( $\delta$ ), lattice parameters (a and c), unit cell volume (V), internal relaxation parameter (u) and bond length ( $b_1$ ) and thickness (t) of the thin films of undoped ZnO, N monodoped ZnO and Sn–N codoped ZnO.

Sample	D (nm)	$\delta$ ( $\times 10^{15} \text{ m}^{-2}$ )	a (Å)	c (Å)	V ( $\times 10^{-30} \text{ m}^3$ )	u	$b_1$ (Å)	t ( $\mu\text{m}$ )
Undoped ZnO	24.08	1.72	3.2469	5.2289	47.74	0.378	1.979	0.483
N doped ZnO	20.91	2.28	3.2507	5.2364	47.92	0.378	1.982	0.568
Sn–N codoped ZnO	11.69	7.32	3.2618	5.2113	48.02	0.381	1.985	0.521

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