

## P-TYPE ZINC OXIDE NANO-STRUCTURE UNIFORM THIN FILM DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE: NITROGEN PORTION VARIATION AT PRECURSOR SOLUTION

S. GOLSHAHI\*, S.M. ROZATI

*Physics Department, University of Guilan, 41335 Rasht, Iran*

Thin films of nitrogen doped zinc oxide (ZnO:N) with different nitrogen to zinc atomic ratio (N/Zn) have been deposited by the spray pyrolysis technique. N/Zn has been changed from 0.1 to 3. According to the XRD results, the variation of N/Zn reveals that the crystal orientation transition from (002) to (100) and (101) begins at N/Zn = 1, while for N/Zn=3, (002) orientation almost disappears and (100) would be the dominant crystal orientation. Optical properties of ZnO:N thin films demonstrate a drastic diminution of transmission in visible spectra region from N/Zn = 1 to N/Zn = 3. Hall effect measurement studies of ZnO:N thin films confirmed the effective role of N/Zn on changing the type of conductivity from n to p for N/Zn=3. SEM images illustrate that increasing the nitrogen ratio in precursor solution induces a drastic change in the surface morphology from nano scale mono dispersed spherical grains to plume-like one.

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### 1. Introduction

The preparation of p-type ZnO by high conductivity and stability of physical properties during the time in atmosphere has been a hot topic for researchers during the last decades. Fabricating a high quality p-type ZnO solve the bipolarity problem of ZnO and consequently bring more applications in fabricating a homojunction ZnO based light emitting diodes, photo diodes and transparent thin film transistors [1,2].

A solution for the problem of p-type ZnO preparation has been presented by introducing a suitable dopant. Among the candidate dopants, nitrogen has attracted more attentions due to its small defect energy level and less probability for forming dopant related defects [3].

In addition, spray pyrolysis technique due to its simple and inexpensive installation, feasibility of large area growth as well as presence of atmosphere that reduce the formation chance of native donor defect, e.g.: oxygen vacancy, has many advantages over other costly growth techniques.

According to our knowledge, nearly all of the reports on p-type ZnO thin films deposited by spray pyrolysis technique, have selected a high ratio N/Zn = 3 in the precursor solution, but no support has been reported for that choice [4-14].

Necessity of optimizing the N/Zn ratio in precursor solution for ZnO:N thin films prepared by spray pyrolysis is demandable. In this paper the effect of precursor solution N/Zn variation on physical properties of ZnO:N thin films has been studied and it has been tried to show reasonable causes for selecting the high N/Zn ratio on fabricating the p-type ZnO:N thin film .

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\*Corresponding author: golshahi@guilan.ac.ir

## 2. Experimental details

ZnO:N films were deposited using spray pyrolysis technique on soda lime glass substrate. The details about the home-made spray deposition unit have been reported elsewhere [15].

Dehydrated zinc acetate and ammonium acetate were selected as the sources of zinc oxide and nitrogen in precursor solution, respectively. Dehydrated zinc acetate amount was constant for all precursor solutions but ammonium acetate amount varied for controlling the N/Zn atomic ratio from 0.1 to 3. These sources were dissolved in 50 cm<sup>3</sup> of a mixture of distilled water and methanol in the ratio 2:3.

To prevent precipitation, a few drops of acetic acid were added to precursor solution. All of the films have been deposited in the same deposition conditions i.e.: air flow rate of 18 L/m, distance from substrate to nozzle, 25 cm, molar concentration of zinc acetate in precursor solution was 0.4 M and the only variable parameter was the N/Zn portion at precursor solution that has been chosen to be 0.1, 0.25, 0.5, 1, 2 and 3.

The crystalline structure was obtained by means of an X-ray diffractometer with Cu-K $\alpha$  radiation (Philips-pw-1830). The optical properties of ZnO:N thin films was investigated by a UV-visible spectrophotometer (Cary 100 Scan Varian).

Electrical studies were done by the RH 2010 Hall Effect Measurement System (PhysTech). Details on the Hall measurement setup and sample preparing were formerly reported [6].

Scanning electron microscope (SEM) images from ZnO:N thin films were obtained using a Philips XL30.

## 3. Results and discussion

### *Structural properties*

X-ray diffraction pattern of ZnO:N thin films for N/Zn between 0.1 to 3 are depicted in Fig.1. By increasing the N/Zn ratio in precursor solution to 0.5, the intensity of (002) crystal orientation slightly decreases. Increasing N/Zn in precursor solution causes a significant change in crystal orientation.

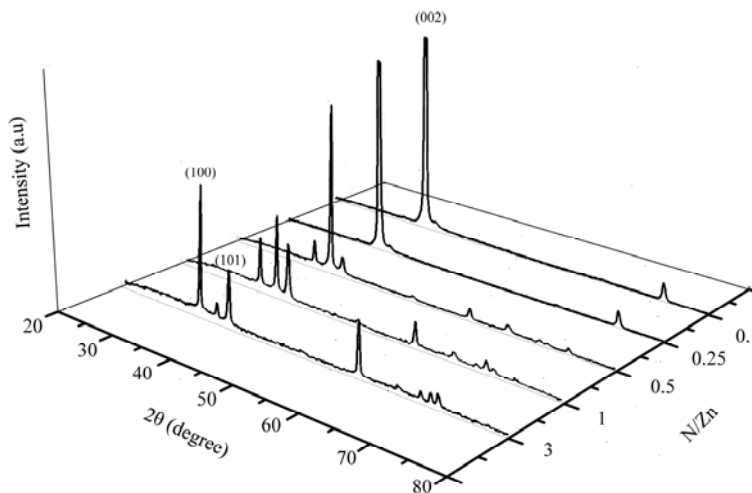


Fig 1. The XRD spectra of the ZnO:N thin films (for N/Zn = 0.1 to 3)

There is a diminution of (002) crystal orientation and the appearance of (100) and (101) which becomes dominant at  $N/Zn=3$ . Similar observation on the appearance of (101) also was reported by Nakano [16]. Increase rate of X-ray diffracted intensity for (100) is higher than for (101). Obtained results suggest that, (100) peak may be a fingerprint of the amount of effective nitrogen incorporation in ZnO and could correspond to Zinc Oxynitrate [17,18].

The mean crystallite sizes of thin films could be obtained by use of Debye-Scherrer's formula [19]. The calculated mean crystallite sizes in ZnO:N thin films, using (002) lattice orientation, were 41.6 nm and 27.7nm for  $N/Zn= 0.25$  and 0.5, respectively. A decrease in crystallite size allows predicting the diminution in mobility of carriers.

As can be seen in Fig.1 by increasing the amount of nitrogen in ZnO, (002) crystal orientation diminishes. Undoubtedly, X-ray diffraction from (002) high intensity in ZnO demonstrate the good crystallinity of the structure and in most of the heavy-doped ZnO compounds, (002) peak intensity increase rate is less than for the other crystal orientations of ZnO [6, 10, 16, 20]. It seems logical to conclude that the incorporation of nitrogen in ZnO destroys the dominant growth of crystallites at c-axis orientation and gives some new crystallites orientations.

### Electrical properties

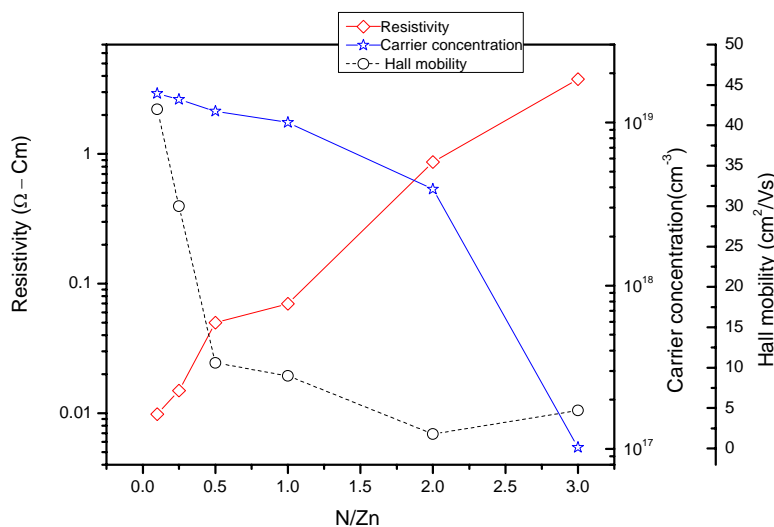


Fig 2. The variation of electrical resistivity, carrier concentration and mobility versus the  $N/Zn$  atomic ratio.

Electrical study has been done by Hall-Effect measurement. Fig. 2 shows the electrical resistivity, carrier concentration and Hall mobility of ZnO:N thin films for various  $N/Zn$  ratios.

Nitrogen must act as an acceptor and replaces oxygen atoms, consequently reducing the total electron concentration by creating holes. But notwithstanding its acceptor role, the low solubility of nitrogen atoms in ZnO will place a part of them as defect centers and donor complexes (e.g.: N-H, N-C and N-N) that decrease the number of effective incorporated nitrogen having acceptor role [21,22].

Finally, according to the Hall-Effect measurements data, increasing the nitrogen amount in precursor solutions only yields a p-type ZnO at  $N/Zn=3$ . It means that the nitrogen incorporation in ZnO must be really low and the real  $N/Zn$  in ZnO film must be very different from the stoichiometric  $N/Zn$  in precursor solution. A strong support to our claim comes from XPS characterization of ZnO:N thin film with a theoretical ratio  $N/Zn=3$  which showed that the real ratio  $N/Zn= 0.07$ , at least at the surface. [22].

Increasing the  $N/Zn$  ratio in precursor solution enhances the resistivity, diminishes the carrier concentration and reduces the Hall mobility. Although we proposed that there is a wide difference between  $N/Zn$  in the precursor solution and in the film, it should be expectable that the

higher is the first, the higher should be the latter. As a consequence, by increasing the N/Zn in precursor solution, nitrogen incorporation rate increases and therefore a carrier concentration reduction should be observed. Hall mobility diminution with N/Zn increase in precursor solution is due to increase of scattering factors caused by enhancing the nitrogen related defects (i.e.: N-N complexes, N-acceptor –native defect complexes)[23]. Although this high amount of nitrogen will preserve its role as a scattering factor, the mobility shows a high increase for N/Zn = 3 its origin being hard to be explained. Decreases in carrier concentration and in Hall mobility, both cause the resistivity enhancement for increasing N/Zn in the precursor solution.

### *Optical properties*

Fig.3 shows the transmission in UV-visible spectra region for ZnO:N thin films for different N/Zn concentration. In complete agreement with our structural and electrical studies, optical transmission carried a drastic diminution for N/Zn=1.

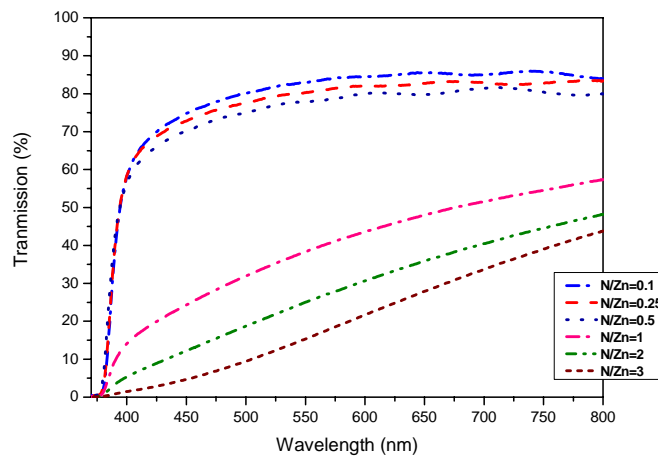


Fig 3. Optical transmission spectra in UV-Visible region of ZnO:N thin films for different N/Zn atomic ratios from 0.1 to 0.3.

According to XRD spectra in Fig.1, ZnO:N obtained from the precursor solution with N/Zn=1 is the sample where a notable transition from (002) (i.e.: the preferential phase of ZnO) to (100) (i.e.: indicator of nitrogen incorporation) occurs. By increasing the nitrogen concentration, a decrease in transparency was observed. Transparency of ZnO:N thin films in the Visible spectra region is as important as its p-type conductivity for their application as a part of an optoelectronic device. Transparency improvement in that region has been achieved by controlling the volume of precursor solution; the optimized results were reported recently [6].

### *Surface morphological properties*

SEM images acquired from ZnO:N thin films for various N/Zn, from 0.1 to 3 have been illustrated in Fig. 4. ZnO:N film prepared with N/Zn = 0.1 exhibits a uniform and smooth surface that is fully covered with dense spherical grains with average diameter of 46 nm. Increasing the N/Zn ratio to 0.25 the surface morphology keeps preserved as well as the grain shape although a slight tendency to agglomeration of grains exists attested by a little enhancement of grain size to 63 nm. At the ratio of N/Zn = 0.5, a similar surface morphology with spherical grains of 90 nm in average is observed and also some clusters that formed by agglomeration of rice like grains with sizes ranging from 400 nm to 1 $\mu$ m are discerned at the surface.

The phenomenon of grains agglomeration may originate from crystallite orientation transition from (002) to (100) since they occur for the same N/Zn ratio. By continuing the N/Zn

ratio increase to 1 or even to 3, surface morphology completely changes and plume like grains with mean sizes ranging from 200 nm to 1  $\mu\text{m}$  cover the nano-spherical grains.

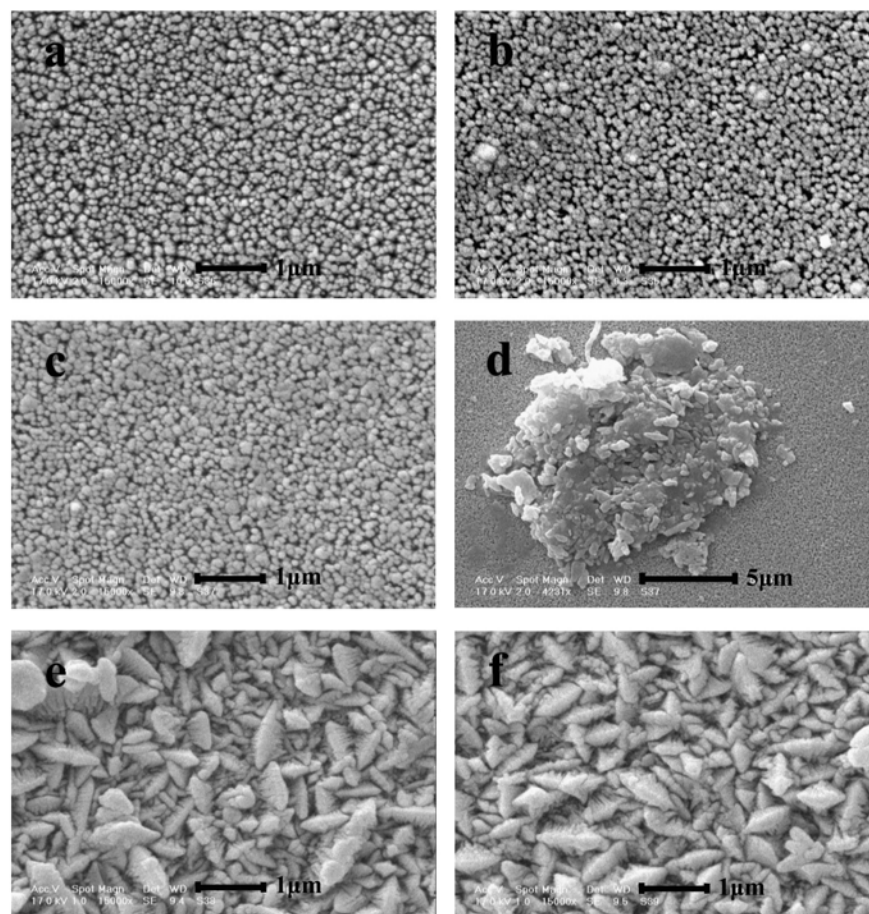


Fig 4. SEM images of ZnO:N thin films prepared at a)  $N/Zn=0.1$ , b)  $0.25$ , c and d)  $0.5$ , e)  $1$  and f)  $3$ .

#### 4. Conclusions

In conclusion, we have investigated the role of nitrogen doping in ZnO structure and studied the effect of a wide range  $N/Zn$  atomic ratio on structural, electrical, optical and morphological surface properties of ZnO:N thin films. Obtained results reveal that the starting point for incorporation of nitrogen in ZnO is  $N/Zn=0.5$  even though the noticeable role of nitrogen in structure starts mainly on  $N/Zn=1$  as shown by the high increase rate of X-ray diffracted intensity from (100) crystal orientation. This peak will be the dominant crystal orientation for  $N/Zn=3$  where a p-type conductivity has been observed contrarily to all the other samples which exhibited a n-type conductivity. The incorporation of nitrogen leads to a drastic increase in resistivity due to the decrease in electron concentration and Hall-mobility. A unique result occurred for  $N/Zn=3$  and that was an enhancement in Hall-mobility which permits the application of this composition to the fabrication of p-type ZnO with high electrical quality. Optical transparency in visible spectra decreases by increasing the effective amount of nitrogen through the ZnO structure.

Surface morphology obtained observed in SEM images for samples prepared at lower  $N/Zn$  ratio illustrate dense spherical grains that convert to rough surface with plume like grains at higher  $N/Zn$  ratios as a consequence of the transition from (002) to (100) crystal orientation.

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