Physica B 490 (2016) 16–20

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

# Effect of nitrogen doping on structural, morphological, optical and electrical properties of radio frequency magnetron sputtered zinc oxide thin films

R. Perumal*, Z. Hassan

*Institute of Nano-Optoelectronics Research and Technology (INOR), School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia*

## ARTICLE INFO

*Article history:*
Received 12 December 2015
Received in revised form
3 March 2016
Accepted 4 March 2016
Available online 5 March 2016

*Keywords:*
Thin film
X-ray diffraction
Optical properties and electrical properties

## ABSTRACT

Zinc oxide receives remarkable attention due to its several attractive physical properties. Zinc oxide thin films doped with nitrogen were grown by employing RF magnetron sputtering method at room temperature. Doping was accomplished in gaseous medium by mixing high purity nitrogen gas along with argon sputtering gas. Structural studies confirmed the high crystalline nature with *c*-axis oriented growth of the nitrogen doped zinc oxide thin films. The tensile strain was developed due to the incorporation of the nitrogen into the ZnO crystal lattice. Surface roughness of the grown films was found to be decreased with increasing doping level was identified through atomic force microscope analysis. The presenting phonon modes of each film were confirmed through FTIR spectral analysis. The increasing doping level leads towards red-shifting of the cut-off wavelength due to decrement of the band gap was identified through UV–vis spectroscopy. All the doped films exhibited p-type conductivity was ascertained using Hall measurements and the obtained results were presented.

## 1. Introduction

The wide band gap semiconductor Zinc oxide (ZnO) receives remarkable attention due to its several attractive physical properties such as large band gap (3.37 eV), high binding energy (60 meV), excellent transparency in the visible region (400–800 nm) and very high conductivity at room temperature [1]. Also, it is one of the most frequently used semiconductor material by its low production cost features. ZnO based optical devices, such as light emitting diodes (LEDs) and laser diodes (LDs) are received considerable attraction due to its excellent optical features [2–3]. In nature, the as grown undoped ZnO thin films exhibit n-type conductivity either due to presenting intrinsic defects such as zinc interstitials ($Z_{ni}$) and oxygen vacancies ($V_O$) or unintentional impurities [4]. It could be enormously increased further by doping donor impurities, such as Al, Ga, In etc., in easier manner. However, it is very important to realize p-type conductivity in ZnO for the development of low cost ZnO based optical devices along with high quality heterojunctions especially for hybrid LEDs. In contrast, achieving p-type conductivity is not as simple as n-type conductivity in the doped ZnO thin films.

Efficient ZnO based devices are realized only when achieved both p-type and n-type conductivities. ZnO exhibits both type of conductivities (n-type and p-type) depend on doping. Nominally, undoped ZnO exhibits n-type conductivity due to the presence of native point defects and their formation energies were calculated using first principles density functional theory (DFT) within the local density approximation (LDA) [5–8]. It is important to obtain p-type behavior, defect free i.e., high quality ZnO should be grown by drastically eliminating the unintentionally presenting donor type defects, which required enormous effects by optimizing the growth parameters. Theoretical predictions strongly suggested that p-type conduction in zinc oxide is achievable. On condition that stable and reproducible p-type conduction requires the acceptor ionization energy must be relatively shallow and minimum compensation by unintentionally presenting donor type impurities and defects. Based on theoretical investigations, growth of p-type ZnO has been realized by doping Group-I element (Li, Na) as well as Group-V elements As or Sb substitution on a zinc site [9–11] or Group-V element substitution on the O site [12]. Also, theoretical predictions explained the other possible route of achieving p-type ZnO by adapting co-doping technique with acceptor and donor as co-dopants, such as N and Al, Ga, or In respectively [13–14]. However, the best choice of p-type doping are nitrogen (N), phosphorus (P) and arsenic (As) have been utilized to achieve p-type ZnO thin films due to its available gaseous sources. Among them, nitrogen was identified as a good candidate for acceptor doping of zinc oxide because of its hazard less nature and

---

* Corresponding author.
*E-mail address:* perumal_cgc@yahoo.co.uk (R. Perumal).

http://dx.doi.org/10.1016/j.physb.2016.03.009
0921-4526/

some papers report on p-type conductivity by doping with nitrogen for obtaining stable and reproducible p-type conductivity that exhibits shallow acceptor by predominantly related to complexes involving nitrogen [15–17]. However, most of the basic aspects of p-type ZnO which was obtained using nitrogen as doping agent are still not well understood and it could well addressed by the proper theoretical model along with proper calculations and that lack of knowledge impedes further progress. Whilst, achievement of stable p-type conductivity in ZnO with sufficient hole concentrations at room temperature is still being challenging [18].

Besides, nitrogen is highly preferred due to its similar ionic radius compared to oxygen and the availability of the various form of gaseous source for achieving p-type conductivity in ZnO structure. Among the available deposition techniques, magnetron sputtering was employed for the growth high-quality p-type ZnO thin films, due to its easiness of gaseous dopant and high deposition rate [19]. In this communication, we report on the effect of nitrogen doping on structural, morphological, optical and electrical properties of radio frequency magnetron sputtered nitrogen doped p-type Zinc oxide thin films and the obtained results were presented.

## 2. Experiment

Nitrogen doped ZnO thin films were synthesized on the commercial 2-in. diameter GaN wafer (from Technologies and Devices International Inc., USA). It was an unintentionally doped n-type GaN (i-GaN) grown on C-plane sapphire substrate. The thickness of GaN film was about 3.0 μm with carrier concentration of about $\sim 4.38 \times 10^{17}$ cm$^{-3}$. The wafer was cleaved into small pieces, were degreased with acetone, 2-propanol and de-ionized water by sonication for five minutes each in sequence and then, dried with high purity hydrogen gas before loaded inside the growth chamber. One micron thick nitrogen doped ZnO thin films were deposited on gallium nitride substrates by employing HHV A500 radio frequency (RF)-sputtering system using ZnO ceramic targets (99.999% purity) at room temperature (no intentional substrate heating) and the maintained power was 150 W. Nitrogen flow rate was varied between 0–10 sccm in steps of 2 sccm (sccm denotes cubic centimeter per minute) through a mass flow controller. The base pressure was $\sim 3 \times 10^{-5}$ mbar that was raised to $\sim 2 \times 10^{-2}$ mbar by purging the chamber with high purity argon and nitrogen gases that served as the sputtering and doping gases respectively and the summary of the growth parameters are tabulated in Table 1. All grown thin films were subsequently annealed in a tube furnace for one hour at 500 °C under nitrogen atmosphere.

Structural characteristics of the deposited nitrogen doped ZnO thin films were studied with X-ray diffraction analysis through PANalytical X'pert X-ray Diffractometer with CuK$_\alpha$ radiation wavelength of 0.154 nm. Surface topography and roughness of the grown films were investigated through atomic force microscope (Model: Dimension Edge, Bruker) respectively. The optical studies

**Table 1**
Summary of the growth parameters.

| Parameters | Values |
|---|---|
| Substrate | i-GaN |
| Targets | ZnO (99.999%) |
| Base pressure | $\sim 3.0 \times 10^{-5}$ mbar |
| Working pressure | $\sim 2.0 \times 10^{-2}$ mbar |
| Substrate temperature | Room temperature (no intentional substrate heating) |
| Ar | 10 sccm |
| N$_2$ | 2 sccm, 4 sccm, 6 sccm, 8 sccm and 10 sccm respectively. |
| ZnO power (RF) | 150 W |

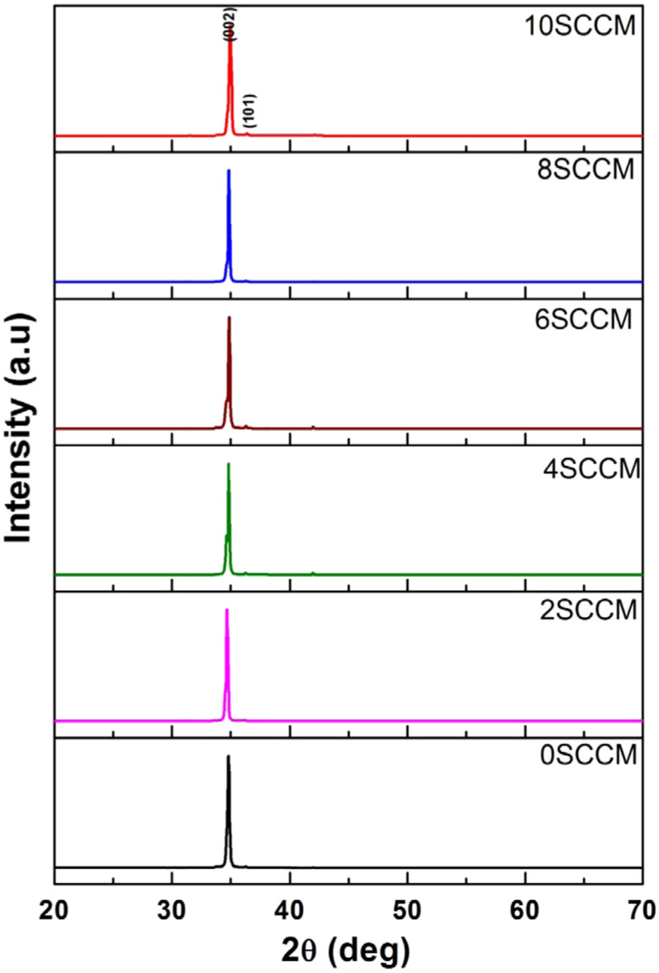

**Fig. 1.** HRXRD patterns of the ZnO and nitrogen doped ZnO films.

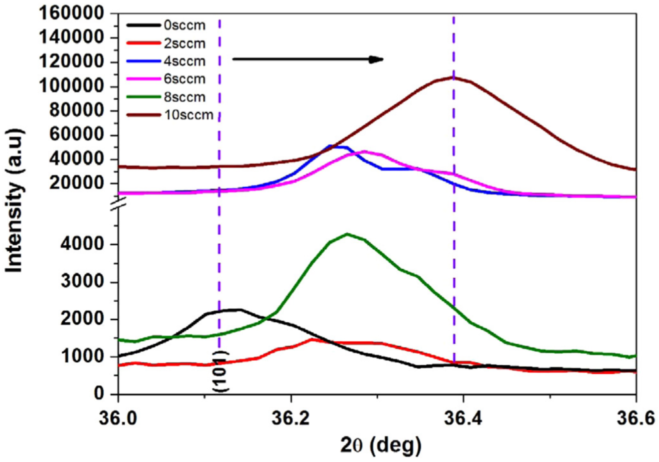

**Fig. 2.** Peak shifts in (101) diffraction plane of the ZnO and nitrogen doped ZnO films.