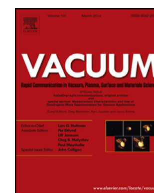
Vacuum 101 (2014) 313–316

Contents lists available at ScienceDirect

Vacuum

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



Rapid communication

Preparation and properties of nitrogen doped *p*-type zinc oxide films by reactive magnetron sputtering

ZhanWu Wang [a,*], Yonggao Yue [b], Yan Cao [b]

[a] Department of Life Sciences, Jilin Normal University, Siping 136000, PR China
[b] Department of Physics, Jilin Normal University, Siping 136000, PR China

ARTICLE INFO

Article history:
Received 20 August 2013
Received in revised form
28 September 2013
Accepted 2 October 2013

Keywords:
ZnO film
Nitrogen doping
Properties
Magnetron sputtering

ABSTRACT

A nitrogen doped zinc oxide (ZnO:N) film was deposited on a quartz substrate at 773 K by reactive radio-frequency (rf) magnetron sputtering using mixture of nitrogen and oxygen as sputtering gas. Hall measurement results indicate that the ZnO:N film behaves *p*-type conduction after annealed at 923 K, which has the lower room temperature resistivity of 2.9 Ω cm, Hall mobility of 18 cm^2/Vs and carrier concentration of 1.3×10^{17} cm^{-3}, respectively. Compositional analysis confirmed the nitrogen (N) is incorporated into the ZnO and the N occupies two chemical states in the ZnO:N. The ZnO:N film has high optical quality and displays the stronger near band edge (NBE) emission in the temperature-dependent photoluminescence spectrum, the acceptor energy level was estimated to be located 110 meV above the valence band. Mechanism of the *p*-type conductivity of the ZnO:N film was discussed in the present work.

© 2013 Elsevier Ltd. All rights reserved.

ZnO is a II–VI compound semiconductor with a wide direct band gap of 3.37 eV at room temperature [1]. It has an exciton binding energy of 60 meV and high exciton emission efficiency, its exciton binding energy is much larger than that of GaN (25 meV). Due to these features, ZnO has been regarded as one of the most promising candidates for the next generation of ultra-violet light-emitting diodes (LED) and laser diodes (LD) [2,3]. In order to realize the potential application of ZnO, the synthesis of high-quality *n*- and *p*-type ZnO film is indispensable. Now, *n*-type ZnO films can be prepared easily, whereas it is difficult to obtain stable and reproducible *p*-type ZnO due to the high self-compensating intrinsic donor defects, the high ionization energy of acceptor impurities, and the low solubility of *p*-type dopants in ZnO [4,5]. Therefore, the preparation of high efficient, reproducible, and stable *p*-type ZnO films has been a bottleneck problem for realizing ZnO based LED and LD. Among the possible dopants for *p*-type ZnO, N is thought to be a promising candidate, which has a similar ionic radius as oxygen [6,7]. Nitrogen has been established as the more soluble group-V impurity, having also the shallowest acceptor level compared to P and As [6]. Based on the theoretical studies [6,7], N is a suitable dopant for producing a shallow acceptor level in ZnO.

In the past years, several nitrogen-doping sources, e.g. N_2 [5,8,9], N_2O [10], NO [11,12], NH_3 [13], CH_3COONH_4 [14] and NH_4NO_3 [15], have been employed to produce *p*-type ZnO samples. The *p*-type ZnO films were deposited by various techniques, such as magnetron sputtering [9], chemical vapour deposition [11,14,15], pulsed laser deposition [12], and molecular beam epitaxy [5]. Although the success in *p*-type concuctivity has been confirmed, however, it is found that the *p*-type ZnO; N generally exhibited unacceptable electrical properties, i.e., low mobility, high resistivity and low carrier concentration et al., which is mainly attributed to that only a small fraction of the incorporated N can be ionized to form the desired shallow acceptors (the ionization energy of $(N)_o$ is observed to be rather deep, i.e., 170–200 meV), therefore, the improvement of *p*-type behaviour is still strongly demanded.

Among the depositing techniques, rf magnetron sputtering present some important advantages like its simplicity and low cost as well as low processing temperature. It is known that substrate properties, sputtering atmosphere, the deposition parameters as well as the post-processing conditions play an important role on the quality of the films. To date, there have little reports about the successful preparation of *p*-type ZnO films by rf magnetron sputtering with N_2–O_2 ambient. In the present work, we prepared the *p*-type ZnO:N film by rf magnetron sputtering using N_2 and O_2 as sputtering gas and the post-annealing techniques, and demonstrated the creation and improvement of *p*-type concuctivity in ZnO:N film, and investigated the structural, electrical and optical

* Corresponding author. Tel./fax: +86 434 3293008.
E-mail address: wangzhanwu@126.com (Z. Wang).

0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.10.001

properties of the ZnO:N film, as well as the formation mechanism of the *p*-type ZnO:N film in details.

The ZnO:N film was fabricated on quartz substrates. The target for the ZnO:N film was prepared by sintering ZnO (99.99% purity) powders at 1000 °C for 10 h in air ambient. The quartz substrates were cleaned in an ultrasonic bath with acetone, ethanol, and deionized water at room temperature, and then washed by deionized water. The vacuum chamber was evacuated to a base pressure of 5×10^{-4} Pa, and then sputtering gases, high purity 32 sccm N_2 (99.99%) and 8 sccm O_2 (99.99%), were introduced with a constant total pressure about 1 Pa. The sputtering power was 120 W. The films were grown on the quartz for 1 h at a substrate temperature of 773 K by rf magnetron sputtering, then annealed for 30 min at a temperature of 923 K under 10^{-4} Pa in a tube furnace. To prevent surface contamination, the film was placed in a quartz boat, which was put into a quartz tube. This quartz tube was then inserted into the furnace.

The structures of the films were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The electrical properties of the films were measured in the van der Pauw configuration by a Hall effect measurement system at room temperature. Compositions and chemical state of elements in the ZnO:N film was detected by X-ray photoelectron spectroscopy (XPS) (ESCALAB MARK II, VG Inc.) using an Al $K\alpha$ as X-ray source. The depth profiles of N, Zn and O were measured by Time-of-Flight secondary ion mass spectrometry (TOF-SIMS). Photoluminescence (PL) measurement was performed at room temperature by the excitation from a 325 nm He–Cd laser.

In order to understand the effect of N doping on ZnO film properties, an undoped ZnO film was grown on a quartz substrate by sputtering of the pure ZnO target with sputtering gas of argon under the same experimental conditions as ZnO:N film used. Hall measurement at room temperature shows that the as-grown ZnO:N and undoped ZnO films both show high resistivity but behave *p*-type and *n*-type conductivity after annealed at 923 K, respectively. Table 1 gives the electrical properties of the ZnO:N and undoped ZnO films obtained by annealing of 923 K. To examine the reliability and repeatability of the conduction of the films, the electrical measurements were performed several times, and much the same results were obtained as expected. As shown in Table 1, the undoped ZnO film exhibits *n*-type conduction, and the ZnO:N film shows *p*-type conduction, the low resistivity of 2.9 Ω cm, high carrier concentration of 1.3×10^{17} cm^{-3} and high hall mobility of 18 cm^2/Vs were acquired at room temperature. It may be attributed to that nitrogen atoms have been doped into the ZnO film as acceptor dopants, which substitute for oxygen in ZnO crystal lattice, forming nitrogen substitute for oxygen (N_o) acceptor, when the concentration of active acceptors exceeds the donor concentration, the ZnO:N film shows *p*-type conduction. The *p*-type characteristics of the ZnO:N film is improved markedly compared with that of the ZnO:N film reported in previous literature [8–15], generally, the previously reported carrier concentration is about 10^{15}–10^{16} order of magnitudes, the mobility is about 10^{-1}–10^{0} order of magnitudes.

Fig. 1 shows the XRD patterns of the undoped ZnO and ZnO:N films annealed at 923 K. It can be observed from Fig. 1 that a strong

Table 1
Electrical properties of ZnO:N and Undoped ZnO films annealed at 923 K at room temperature.

Sample	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vs)	Type
ZnO:N film	2.9	1.3E + 17	18	*p*
Undoped ZnO film	6.8E + 0	1.4E + 19	6.4E-2	*n*

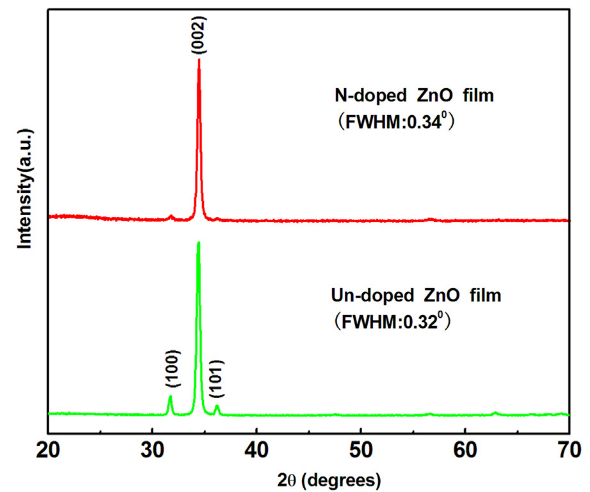


Fig. 1. X-ray diffraction patterns Undoped and ZnO:N films annealed at 923 K.

(002) peak is observed in both patterns, two very small peaks are observed at 2θ of near 31.76°, 36.25°, which are attributed to the diffraction of (100) and (101) planes of ZnO (ICDD card#79-0206), respectively, implying that the undoped ZnO and ZnO:N films have good crystal quality with (002) preferential orientation. No other phases (such as Zn_3N_2) are detected. The full-width at half-maximum (FWHM) of the (002) peak is measured to be 0.32° for the undoped ZnO and 0.34° for the ZnO:N film. This may be due to incorporation of N dopants into the ZnO film can create more defects in the lattice, which indicate degrading crystallinity somewhat. Moreover, the diffraction angle of the (002) peak shifts to higher diffraction angle from 34.41° to 34.47° and the d-spacing value decreases from 2.606 to 2.601 Å. In addition, the lattice constant obtained from the (200) diffraction peak for undoped film is 5.212 Å, while the lattice constant obtained from ZnO:N film is 5.204 Å. The variation is attributed to N atoms substitute for O atoms in the ZnO crystal lattice, which leads to the formation of the bonds of Zn–N in the ZnO:N film. Since Zn–N bond length is somewhat smaller than Zn–O bond length [6], therefore, d-spacing value and the lattice constant for the ZnO:N film became smaller than that of undoped ZnO film, which agrees with the high diffraction angle.

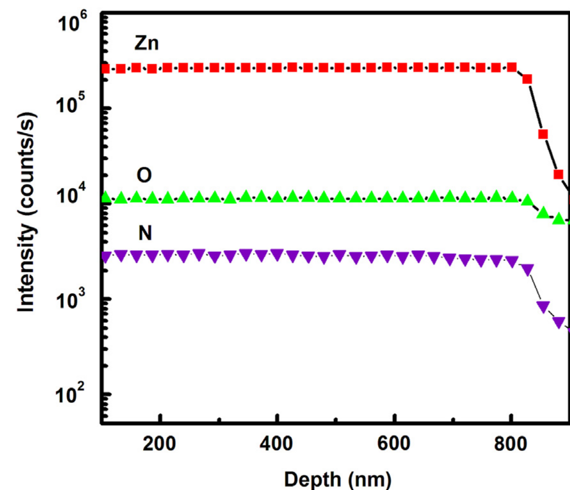


Fig. 2. SIMS depth profiles of the ZnO:N film annealed at 923 K.

Download English Version:

https://daneshyari.com/en/article/8045087

Download Persian Version:

https://daneshyari.com/article/8045087

Daneshyari.com