Thin Solid Films 518 (2010) 3289–3292

Contents lists available at ScienceDirect

Thin Solid Films

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

Growth ambient dependent electrical properties of lithium and nitrogen dual-doped ZnO films prepared by radio-frequency magnetron sputtering

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ARTICLE INFO

Article history:
Received 16 January 2009
Received in revised form 22 August 2009
Accepted 4 September 2009
Available online 16 September 2009

Keywords:
Semiconductors
Zinc oxide
Electrical properties and measurements
Photoluminescence

ABSTRACT

Lithium (Li) and nitrogen (N) dual-doped ZnO films with wurtzite structure were prepared by radio-frequency magnetron sputtering ZnO target with Li_3N in growth ambient of pure Ar and the mixture of Ar and O_2, respectively, and then post annealing techniques. The film showed week p-type conductivity as the ambient was pure Ar, but stable p-type conductivity with a hole concentration of $3.46\times10^{17}\,cm^{-3}$, Hall mobility of 5.27 cm^2/Vs and resistivity of 3.43 Ω cm when the ambient is the mixture of Ar and O_2 with the molar ratio of 60:1. The stable p-type conductivity is due to substitution of Li for Zn (Li_{Zn}) and formation of complex of interstitial Li (Li_i) and substitutional N at O site, the former forms a Li_{Zn} acceptor, and the latter depresses compensation of Li_i donor for Li_{Zn} acceptor. The level of the Li_{Zn} acceptor is estimated to be 131.6 meV by using temperature-dependent photoluminescence spectrum measurement and Haynes rule. Mechanism about the effect of the ambient on the conductivity is discussed in the present work.

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1. Introduction

ZnO, a II–VI compound semiconductor, is considered as a promising material for ultraviolet (UV) light-emitting diodes, laser diodes and photodetectors [1], due to its many excellent physical properties, such as a wide band gap of 3.37 eV and a large excitonic binding energy of 60 meV at room temperature. To realize application of ZnO-based devices, preparation of n-type and p-type ZnO with good conductivity and high quality is necessary. It has been proven that stable n-type ZnO films can be prepared easily, however, stable and reproducible p-type ZnO film is fabricated difficultly. Therefore, study on preparation and properties of the p-type ZnO thin film has become a very important issue. In the recent years, many p-type dopants, such as nitrogen (N), phosphorus, arsenic, antimony (Sb) and lithium (Li), were employed to prepare the p-type ZnO films. Among these dopants, Li and N are considered as the best candidates for producing p-type ZnO due to small strain effects and shallow acceptor levels of substitution of Li for Zn (Li_{Zn}) and N for O (N_O), based on first-principle calculation [2]. In order to improve the stability and electrical properties of p-type ZnO, several groups tried to fabricate Li–N dual-doped ZnO (denoted as ZnO: (Li, N)) by various techniques such as radio-frequency (rf) magnetron sputtering [3,4], two-step heat treatment [5], pulsed laser deposition [6,7], and plasma-assisted molecular-beam epitaxy (PA-MBE) [8]. Ko et al. [8] obtained n-type ZnO: (Li, N) by PA-MBE technique using Li_3N as Li and N dopants, however, Ye et al. fabricated the ZnO: (Li, N) films with good p-type conduction [6,7]. Our group also obtained the p-type ZnO: (Li, N) films with high resistivity and low hole density [3–5]. Although p-type ZnO: (Li, N) films have been investigated widely, its electrical and optical properties still need enhancement, and the mechanism of the p-type conductivity is not clear yet.

In the present work, p-type ZnO: (Li, N) film was fabricated by rf-magnetron sputtering and post annealing techniques, and the electrical and optical properties as well as formation mechanism of the p-type ZnO: (Li, N) were investigated.

2. Experimental procedures

A ZnO: (Li, N) target with nominal content of 2 at.% Li and 0.67 at.% N was fabricated by sintering mixture of 99.99% pure Li_3N and ZnO powders at 300 °C for 2 h firstly and then 750 °C for 10 h in air ambient. Quartz substrates were treated with acetone, ethanol and deionized water in an ultrasonic bath to remove surface contaminations, and then blown dry using high-purity N_2. The growth chamber was evacuated to a base pressure of 5×10^{-4} Pa and then filled with flow of 99.999% pure Ar or a mixture of 99.999% pure Ar and 99.999% pure O_2 with the molar ratio of Ar to O_2 of 60:1 up to 1.0 Pa, and this pressure was maintained during the growing process. ZnO: (Li, N) films were grown on quartz substrates at 500 °C by rf-magnetron sputtering the ZnO: (Li, N) target using the pure Ar and the mixture, respectively. And these two films were denoted as sample (A) and sample (B). The as-grown films were annealed in vacuum for 30 min at 600 °C.

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0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.09.008

Crystal structure of the films was identified by rotation anode X-ray diffractometer (XRD) (Rigaku D/Max-RA) with CuKα1 radiation ($\lambda = 0.15418$ nm), the scan step size is 0.02°, and error is within ± 0.0001 nm for lattice constant measurement from a statistic viewpoint. The compositions of ZnO: (Li, N) film were detected by time-of-flight secondary ion mass spectrometry (TOF-SIMS) (TOF-SIMS IV instrument from IONTOF Gmbh). The electrical properties were investigated by Hall measurement in the Van der Pauw configuration at room temperature and magnetic fields of 0.3–1.5 T (Lakershore HMS 7707). The results were averaged to compensate for various electromagnetic effects. Electrodes were fabricated by depositing metal indium on the surface of films and annealing at a pressure of ~10^{-3} Pa. Ohmic contact between the indium spots and film was confirmed prior to Hall measurement. The photoluminescence (PL) measurement was performed in a temperature ranging from 82.7 to 300 K by the UV Labran Infinity Spectrophotometer, which is excited by the 325 nm line of a He–Cd laser with a power of 50 mW.

3. Experimental results and discussion

Fig. 1(a) and (b) shows XRD patterns of sample (A) and sample (B), respectively. Fig. 1(a) indicates that there are three diffraction peaks of (002), (100) and (101) planes in the XRD profile of the sample (A), while there is only one strong (002) diffraction peak in the XRD profile of the sample (B), as shown in Fig. 1(b). These results imply that the sample (B) has preferential orientation in *c*-axis direction. The diffraction angle 2θ of the (002) peaks is 34.52° for sample (A) and 34.49° for sample (B), as shown in the inset of Fig. 1. Using the 2θ value of the (002) peaks and the formula: $c = \lambda / \sin(\theta)$, for (002) peak of ZnO, where *c* is lattice constant in *c* axis and θ is diffraction angle of (002) peak, the *c* is calculated to be 0.5196 nm for sample (A) and 0.5201 nm for sample (B). *c* values of samples (A) and (B) are smaller than that of nominally undoped ZnO films prepared under the same growth and anneal conditions as samples (A) and (B), which are 0.5205 nm and 0.5211 nm, respectively. These results imply that Li and N incorporated into ZnO and led to decrease in the lattice constant *c*.

In order to further confirm whether Li and N were doped in the ZnO and investigate distribution of them in the sample, TOF-SIMS measurement was performed. Fig. 2 shows a TOF-SIMS depth profile of sample (B), indicating that Li and N are incorporated into ZnO and uniformly distributed in the film. Both XRD and TOF-SIMS demonstrate that Li and N are doped in ZnO, and form a Li–N co-doped ZnO film.

The Hall measurements at room temperature indicate that both the as-grown undoped ZnO and ZnO: (Li, N) films behave insulating conductivity, but semiconductivity after annealed at 600 °C. The transition of the electrical properties induced by annealing may be attributed to the following factors: (1) improvement of the crystal quality of the films, (2) activation of the doped elements or native defects, and (3) escape of H from ZnO for p-type ZnO produced by annealing [9]. Table 1 gives electrical properties of various films obtained by annealing at 600 °C. As shown in Table 1, the undoped ZnO film shows n-type conductivity, sample (A) shows weak p-type conductivity, which means that conductivity type alters irregularly as applied magnetic field changes during measurement process, and sample (B) behaves good p-type conductivity with a hole concentration of 3.46×10^{17} cm^{-3}, Hall mobility of 5.27 cm^2/Vs, and resistivity of 3.43 Ω cm. These results imply that the p-type conductivity of ZnO: (Li, N) is related to Li and N doping [10]. Fig. 3 shows the electrical properties of the sample (B) as a function of preservation period in air ambient, which indicates that the p-type conductivity of the film is well maintained in the period of 50 days. However, the sample (A) transforms from p-type to n-type semiconductor after preservation for a few days. The results mentioned above indicate that sample (B) possesses more stable and better p-type conductivity.

It is known that substitutional Zn at O site, zinc interstitial (Zn_i), oxygen vacancies, interstitial Li (Li_i), and Li_{Zn}–Li_i complex are donors, while zinc vacancy (V_{Zn}), interstitial oxygen (O_i), Li_{Zn} and N_O are acceptors. Comparing with the nominally undoped ZnO film, the weak p-type conductivity of sample (A) may be ascribed to the following factors: (i) formation of acceptors induced by the dopant of Li_3N, such as Li_{Zn} and N_O, (ii) existence of some V_{Zn}, and (iii) existence of some intrinsic defects and Li_i donors. Differing from growth ambient of sample (A), sample (B) is fabricated in mixture of Ar and O_2 with a mole ratio of 60:1, and shows more stable and better p-type conductivity than sample (A). This means that O_2 participation in the growth ambient benefits improvement of p-type conduction,

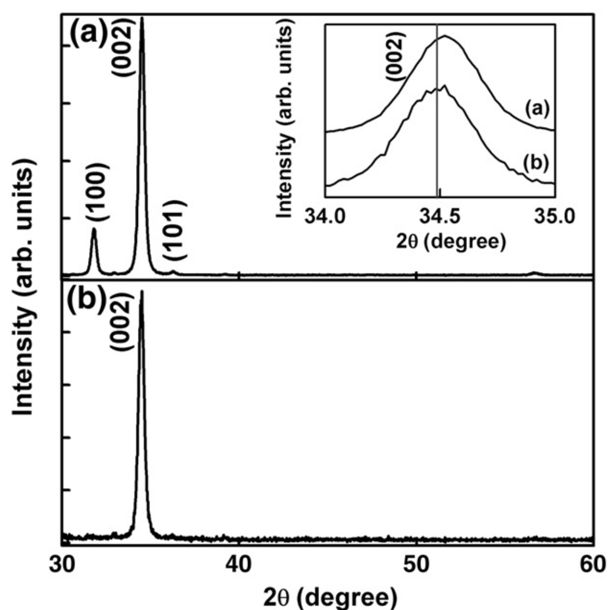

Fig. 1. XRD patterns of ZnO: (Li, N) thin films grown in (a) pure Ar and (b) the mixture of Ar and O_2 with mole ratio of Ar to O_2 of 60:1. The inset is the corresponding XRD profile in diffraction angles (2θ) of 34–35°.

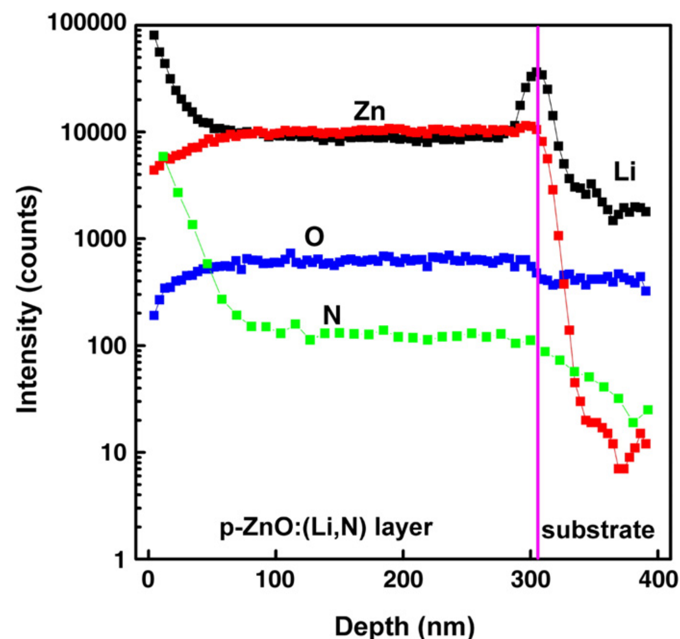

Fig. 2. TOF-SIMS depth profile of the ZnO: (Li, N) thin film grown in the mixture of Ar and O_2 with mole ratio of Ar to O_2 of 60:1.

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