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Influence of annealing temperature on properties of nitrogen-doped zinc oxide films deposited by magnetron sputtering

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ABSTRACT

Nitrogen-doped *p*-type zinc oxide films have been realized by radio frequency (rf) magnetron sputtering and post-annealing techniques. The effect of annealing temperature on the structural, electrical and optical properties of nitrogen-doped zinc oxide films was investigated by X-ray diffraction, Hall-effect, photoluminescence measurements. The nitrogen-doped *p*-type zinc oxide film with good structural, electrical and optical properties can be obtained at an intermediate annealing temperature region (e.g., 650 °C). The nitrogen-doped *p*-type zinc oxide had the lowest resistivity of 2.9 Ω cm, Hall mobility of 18 cm^2/Vs and carrier concentration of 1.3×10^{17} cm^{-3}. The *p*-type conduction behavior of the nitrogen-doped zinc oxide film was confirmed by the rectifying *I–V* characteristics of a ZnO homojunction. The chemical bonding states of nitrogen doped in ZnO film were examined by XPS analysis. Mechanism of the *p*-type conductivity was discussed in the present work.

1. Introduction

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 larger than that of GaN and high exciton emission efficiency. Due to these features, ZnO has become a promising candidate for applications in blue and ultraviolet (UV) light sources and as a UV detector [2–5]. Its practical applications in these fields

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depend on the fabrication of ZnO *p*–*n* homo-junctions. High quality *n*-type ZnO has been achieved by doping with group III elements such as Al, Ga and In [6,7]. However, it is difficult for ZnO to achieve *p*-type conduction due to the high activation energy and low solubility of acceptor doping. Possible acceptor dopants include Group-V (N, P, and As) and Group-I elements (Li, Na). However, among the possible dopants for *p*-type ZnO, N substituting for O appears the most promising choice because of its similar atomic radius and low-activation energy compared to other Group-V elements [8–14]. Many workers have attempted to produce *p*-type nitrogen-doped ZnO films [15,16]. However, the poor quality of the *p*-type ZnO films still constitutes an impediment for the progress in device performances.

To enhance the luminescence of ZnO homo-junction, more attention needs to be paid in improving the crystallinity of ZnO films and decrease the background carrier concentration. It is shown very often that annealing is a suitable and effective process to improve the crystallinity of semiconductor films and decrease the background carrier concentration. Post-annealing greatly affects the film properties, such as crystal quality, electric behavior and luminescent property. The effects of annealing temperature on the properties of ZnO film are very great, and the as-grown films grown by the same processing annealed in different temperature usually have different changing behaviors. In this work, *p*-type ZnO films were prepared using nitrogen doping by rf magnetron sputtering in N_2–O_2 ambient. Meanwhile, the effects of post-annealing temperature on the crystal quality, electrical and luminescent properties of N-doped ZnO films are studied in details.

2. Experimental procedures

The N-doped ZnO films were fabricated on quartz substrates by rf magnetron sputtering technique using nitrogen and oxygen as sputtering gas. The target for the N-doped ZnO 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 de-ionized water at room temperature, and then washed by de-ionized 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 films were grown on the quartz for 1 h at a substrate temperature of 500 °C by rf magnetron sputtering, then annealed for 30 min at different temperature 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.

XRD analysis was performed by rotation anode X-ray diffractometer (XRD) (Rigaku D/Max-RA) with Cu Kα_1 radiation ($\lambda = 0.15406$ nm), the scan step size used is 0.02°, and error is within ±0.0003 nm for lattice constant measurement. The power of XRD is 18 KW. The electrical properties of the films were measured in the van der Pauw configuration by a Hall effect measurement system at room temperature. X-ray photoelectron spectroscopy (XPS) analysis were performed by a spectrometer (ESCALAB MARK II, VG Inc.) using an Al $K\alpha$ as X-ray source with a base pressure of 10^{-8} Pa in the analysis chamber. The N-doped ZnO film was cleaned by sputtering with Ar ion bombardment for 2 min prior to XPS measurement. Studies of the narrow scan regions acquired enabled us to obtain the chemical states and the quantitative composition on surfaces after sputtering. All narrow scan spectra showed a peak shift due to the electrostatic charging of the surface layer. It was corrected considering the increment registered on the surface C–C/C–H peak position, with respect to the literature value of 284.6 eV. The depth profiles of P, 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.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the N-doped ZnO films deposited at 500 °C and annealed at 600 °C, 650 °C, 750 °C and 800 °C under 10^{-4} Pa, respectively. It can be observed from Fig. 1 that a strong (002) peak is observed in all 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