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Effect of annealing temperature on structural, electrical and optical properties of B–N codoped ZnO thin films

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ABSTRACT

The B–N codoped *p*-type ZnO thin films have been prepared by radio frequency magnetron sputtering using a mixture of nitrogen and oxygen as sputtering gas. The effect of annealing temperature on the structural, electrical and optical properties of B–N codoped films was investigated by using X-ray diffraction, Hall-effect, photoluminescence and optical transmission measurements. Results indicated that the electrical properties of the films were extremely sensitive to the annealing temperature and the conduction type could be changed dramatically from *n*-type to *p*-type, and finally changed to weak *p*-type in a range from 600 °C to 800 °C. The B–N codoped *p*-type ZnO film with good structural, electrical and optical properties can be obtained at an intermediate annealing temperature region (e.g., 650 °C). The codoped *p*-type ZnO had the lowest resistivity of 2.3 Ω cm, Hall mobility of 11 cm^2/Vs and carrier concentration of 1.2×10^{17} cm^{-3}.

1. Introduction

ZnO has attracted much attention as a promising material for short-wavelength optoelectronic devices, such as light emitting diodes and laser diodes, because of its wide band gap of 3.37 eV, large exciton binding energy (60 meV), and high optical gain (320 cm^{-1}) at room temperature [1,2]. To realize the light-emitting devices, an important issue is the fabrication of *p*-type ZnO with a high hole concentration and a low resistance. However, it is difficult to achieve low resistivity *p*-type conduction for ZnO film due to problems such as self-compensation, deep acceptor level, and low solubility of the acceptor dopants [3]. Among the possible dopants for *p*-type ZnO, N is thought to be a promising candidate, which has a similar ionic radius as oxygen [4,5]. Nitrogen has been established as the more soluble group-V impurity, having also the shallowest acceptor level compared to P and As [4]. However, N monodoping (MD) creates a rather deep acceptor level, which is unfavorable for doping [6]. On the other hand, the low solubility of N MD may not create a sufficient number of holes to compensate the free electrons in order to obtain *p*-type ZnO [6].

Fortunately, the codoping method using acceptor (e.g., N) and donors (e.g., B, Al, Ga, or In) simultaneously was suggested theoretically as a possible means to enhance nitrogen solubility in ZnO and to lower its ionization energy [7–9]. The theoretical calculation indicates that *p*-type doping using N species increases the Madelung energy while *n*-type doping using group III elements (B, Al, Ga and In species) decreases the Madelung energy. Therefore, the simultaneous codoping (III elements and N species) decreases the Madelung energy of *p*-type codoped ZnO compared with *p*-type ZnO doped with the N acceptor alone. Moreover, the theoretical calculation also indicates that the simultaneous codoping using reactive donor codopants, Al, Ga, In and B, not only enhances the incorporation of N acceptors but also gives rise to shallower N-acceptor level in the band gap in *p*-type codoped ZnO. Recently experimental investigation related to the codoping techniques, such as Al–N [10,11], Ga–N [12,13], and In–N [14,15], has been reported in several literatures, meanwhile, several codoping techniques have been utilized to prepare *p*-type ZnO films, such as the codoping of nitrogen and gallium by pulse laser deposition, nitrogen and beryllium by radio frequency (rf) sputtering, etc. [16,17]. However, preparation of *p*-type ZnO using B–N codoping method was little reported by far. In our previous work [18], we used rf magnetron sputtering to prepare B–N codoped ZnO films and obtained *p*-type ZnO in N_2–O_2 sputtering ambient, meanwhile, the *p*-type conduction mechanism of the B–N codoped ZnO film has been discussed.

It is well known that post-annealing greatly affects the film properties, such as crystal quality, electric behavior and luminescent property. The annealing temperature usually has strong influence on the properties of ZnO thin film. That is to say, post-annealing the as-grown films at different annealing temperature usually induces

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different changing behaviors of properties. In this work, *p*-type ZnO films were prepared using the B–N codoping by rf magnetron sputtering in N_2–O_2 ambient. Meanwhile, the effect of post-annealing temperature on the properties of B–N codoped ZnO films was studied in detail.

2. Experimental procedures

B–N codoped ZnO films, as well as N-doped ZnO films, were fabricated on quartz substrates by rf magnetron sputtering technique using nitrogen and oxygen as sputtering gas. The target for B–N codoped films was prepared by sintering mixture of ZnO (99.99% purity) and 1 at.% BN (99.99% purity) powders at 1000 °C for 10 h in air ambient. The target for N-doped films 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 gasses, high purity 8 sccm N_2 (99.99%) and 32 sccm O_2 (99.99%) (sccm denotes cubic centimeter per minute at standard temperature and pressure), were introduced with a constant total pressure about 1 Pa. The films were grown on the quartz for 1 h at 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 films were placed in a quartz boat, which was put into a quartz tube. This quartz tube was then inserted into the furnace. The film thickness can be estimated to be about 700 nm by field-emission scanning electronic microscope (FESEM, Hitachi S-4800). The operating voltage is 15 kV.

The structures of the films were characterized by X-ray diffraction (XRD). XRD analysis was performed by rotation anode X-ray diffractometer (XRD) (Rigaku D/Max-RA) with Cu $K\alpha_1$ 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 obtained by Hall measurement in the Van der Pauw configuration at room temperature using a current of 300 nA 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 films was confirmed prior to Hall measurement. Photoluminescence measurement was performed at room temperature by the excitation from a 325 nm He–Cd laser. The room-temperature absorption measurement was performed using an UV–VIS–near infrared (NIR) spectrophotometer (Shimadzu, Kyoto, Japan). The depth profiles of B, N, Zn and O were measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS) with Cs^+ as the primary ion, an accelerating voltage of 3 kV, and a beam current of 12 nA. The time-of-flight detector of secondary ions has a high mass resolution above 7000, depth profiles can be measured with resolution of 1 nm.

3. Experimental results and discussions

Hall effect measurements were applied to characterize the electrical properties of the ZnO films annealed at different temperature and the corresponding results are listed in Table 1. 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, as the annealing temperature is increasing up from 600 to 800 °C, the conductivity of the film changed dramatically from *n*-type to *p*-type, and finally changed to weak *p*-type. At annealing temperature of 600 °C, the concentration of the donor exceeds the acceptor concentration, the conduction type shows *n*-type. It may be due to the increase of annealing temperature, zinc interstitials (Zni) and some nitrogen atoms as interstitial atoms can be escaped from the films, so that the density of acceptor will be dominant, and the ZnO is inverted from *n*-type to *p*-type. When annealing temperature increases to 800 °C, some nitrogen atoms substituting for oxygen, which serve as acceptor dopants in ZnO crystal lattice, may be escaped from the films. Thus, the proportion of N atoms as acceptors take part in the hole conductivity will decrease. Therefore, the conduction type shows weak *p*-type, and the concentration of holes carries decreases, correspondingly the resistivity increases. At the intermediate temperature of 650 °C, B–N codoped *p*-type ZnO film with good electrical properties can be obtained with the lowest resistivity of 2.3 Ω cm, Hall mobility of 11 cm^2/Vs and carrier concentration of 1.2×10^{17} cm^{-3}. Table 1 also shows the electrical properties of the N-doped ZnO film prepared under the same experimental conditions as B–N codoped ZnO film and annealed at 650 °C, which indicates *p*-type conduction, but it is evidently worse than that of the B–N codoped film. The good *p*-type conduction for the codoped film may be ascribed to the enhancement of N in ZnO due to the presence of B in the film.

Table 1
Electrical properties of B–N co-doped and N-doped ZnO films at room temperature.

Samples	Annealing temperature (°C)	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility ($cm^2V^{-1}s^{-1}$)	Type
B–N co-doped films	600	1.2	3.9E+19	1.2E−1	n
	650	2.3	1.2E+17	11	p
	700	4.6	1.5E+17	8.7	p
	800	2.8E+3	2.1E+14	13	p/n
N-doped film	650	5.0E+1	3.6E+16	4.4	p

In order to further verify the *p*-type conduction of the B–N codoped ZnO film annealed at 650 °C, a ZnO homojunction is synthesized by depositing undoped *n*-ZnO layer on the B–N co-doped *p*-ZnO layer, and its *I*–*V* characterization is investigated and shown in Fig. 1. The schematic structure of the ZnO *p*–*n* homojunction is illustrated in the lower right inset. The indium and Ni/Au electrodes are used to form Ohmic contacts with the *n*-type and *p*-type layers, respectively. In order to obtain good Ohmic contacts between the ZnO films and the electrodes, the contacts are rapidly annealed at 673 K for 3 min and 5 min, respectively. As shown in the upper left inset, the linear behavior of *I*–*V* curves measured from both Ni/Au on *p*-type and In on *n*-type demonstrates the Ohmic nature of the contacts. Moreover, from Fig. 1, it is clearly observed that *I*–*V* curves of homojunctions exhibit typical

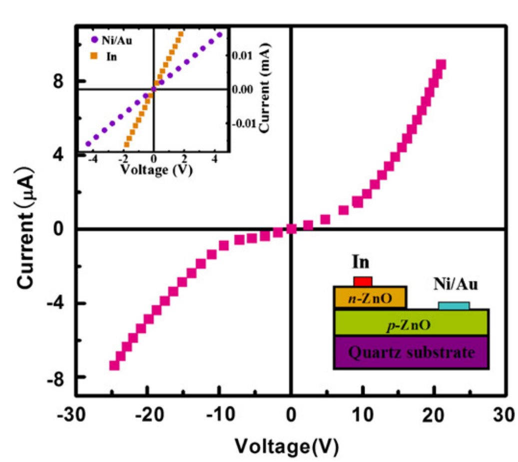

Fig. 1. *I*–*V* characteristics of the homojunction composed of undoped *n*-ZnO and B–N codoped *p*-ZnO annealed at 650 °C. The lower right inset shows the schematic structure of the *p*–*n* heterojunction. The upper left inset shows the Ohmic contact characteristic of two Ni/Au contacts on the *p*-type and two In contacts on the *n*-type ZnO.