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Fabrication and properties of B–N codoped p-type ZnO thin films

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Abstract

A p-type B–N codoped ZnO film was grown on quartz by magnetron sputtering and post-annealing techniques. It has room-temperature resistivity of 2.3Ω cm , Hall mobility of $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and carrier concentration of $1.2 \times 10^{17} \text{ cm}^{-3}$, better than the electrical properties of the N-doped p-type ZnO. The ZnO homojunction fabricated by deposition of an undoped n-type ZnO layer on the B–N codoped p-type ZnO layer showed clear p–n diode characteristics. Differing from the N-doped ZnO, the low-temperature photoluminescence spectrum of the codoped ZnO film consists of two dominant peaks located at 3.096 eV and 3.251 eV, respectively. The former is due to radiative electron transition from the conduction band to the Zn vacancy acceptor level, and the latter due to recombination of the donor–acceptor pair. The mechanism of p-type conductivity was discussed in this work.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO has attracted much attention as a promising material for short-wavelength optoelectronic devices, such as lightemitting 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 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 the ZnO film because of problems such as self-compensation, deep acceptor level and low solubility of the acceptor dopants [3]. Among possible acceptor dopants, nitrogen is similar to O in terms of the atomic size and produces a shallow acceptor lever in ZnO, long been considered as a possible acceptor dopant for p-type ZnO [4]. However, since the formation enthalpy of $-348.28 \text{ kJ mol}^{-1}$ [5] for ZnO is significantly lower than that of -20 kJ mol^{-1} for Zn_3N_2 [6], the formation of Zn–O bonds is energetically favourable compared with that of Zn–N bonds. This suggests a low solubility of N into ZnO as N monodoping. The low solubility may not create a sufficient number of holes to compensate the free electrons to form p-type ZnO [7].

The codoping method using acceptors (e.g. N) and donors (e.g. B, Al, Ga, or In) simultaneously was suggested theoretically as a possible means to enhance the nitrogen solubility in ZnO and to lower its ionization energy [7–10]. Recently experimental investigations related to codoping techniques, such as Al–N [11, 12], Ga–N [13, 14] and In–N [15, 16], have also appeared in several publications; meanwhile, several codoping techniques have been reported to prepare p-type ZnO films, such as the codoping of nitrogen and gallium by pulse laser deposition and nitrogen and beryllium by radio frequency (rf) sputtering [17, 18]. However, no successful preparation of p-type ZnO using the B–N codoping method has been reported so far. In this work, the p-type ZnO film was prepared using B–N codoping by rf magnetron

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sputtering in N_2 – O_2 ambient. Meanwhile, the mechanism of p-type conductivity was investigated.

2. Experimental procedures

Two series of films, B-N codoped and N-doped ZnO films, were prepared on a quartz substrate using a mixture of oxygen and nitrogen as the sputtering gas by the rf magnetron sputtering technique. The target for the codoped film was prepared by sintering a 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 the N-doped 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 using de-ionized water. The vacuum chamber was evacuated to a base pressure of 5×10^{-4} Pa, and then sputtering gases, high purity 8 sccm N_2 (99.99%) and 32 sccm O_2 (99.99%) (sccm denotes cubic centimetre per minute at STP), were introduced with a constant total pressure of about 1 Pa. 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 923 K under 10^{-4} Pa in a tube furnace. The film thickness can be estimated to be about 700 nm by field-emission scanning electronic microscopy (FESEM).

The structures of the films were characterized by x-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The electrical properties were measured in the van der Pauw configuration by a Hall effect measurement system at room temperature. The depth profiles of B, N, Zn and O were measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The photoluminescence (PL) measurement was performed at room temperature by the excitation from a 325 nm He–Cd laser.

3. Results and discussion

It has been demonstrated that N-doped p-type ZnO can be fabricated by magnetron sputtering or molecule beam epitaxy techniques using O_2 and N_2 mixed gas [19, 20]; however, preparation of B–N codoped p-type ZnO has not been reported to date. In order to detect the composition of the ZnO film prepared by sputtering the target consisting of ZnO and 1 at% BN using a mixture of O_2 and N_2 , SIMS measurement was performed, and the depth profile of B, N, Zn and O in the ZnO film is shown in figure 1. It is evident that B and N have been clearly detected, and their concentration profiles are quite flat throughout the film depth, which indicates that B and N have been uniformly doped into ZnO to form a B–N codoped ZnO film.

Figure 2 shows the XRD patterns of the B–N codoped and N-doped ZnO films, where only diffraction peaks of ZnO with a wurtzite structure are observed and the dominant diffraction peak is the (002) diffraction peak, indicating that both the ZnO films only consist of ZnO with (002) preferential orientation and no other phases (such as BN or Zn₃N₂) exist. The full-width at half-maximum (FWHM) of the (002) peak



Figure 1. (Color online) SIMS depth profiles of B–N codoped ZnO films.



Figure 2. (Color online) XRD patterns of B–N codoped and N-doped ZnO films deposited on a quartz substrate.

is measured to be 0.44° for B–N codoped ZnO and 0.28° for N-doped ZnO. The FWHM of B–N codoped ZnO is larger than that of N-doped ZnO, which is similar to the results observed in Al–N and Ga–N codoped ZnO. According to codoping theory, the presence of B (or Al or Ga) can facilitate incorporation of N into ZnO, resulting in that impurities and native defects are more in B (Al, Ga)–N codoped ZnO than in N-doped ZnO. Therefore, the crystal quality of codoped ZnO is usually worse than that of N-doped ZnO, and the FWHM of the codoped ZnO is wider than that of N-doped ZnO, as observed in this work.

The Hall measurement at room temperature shows that the as-grown B–N codoped and N-doped ZnO show high resistivity but show p-type conductivity after annealing at 923 K. The transition of the electrical properties from high resistivity to p-type conduction may be attributed to two factors, one is improvement in the crystal quality, and another

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

Sample	Resistivity (Ω cm)	Carrier concentration (cm ⁻³)	Mobility ($cm^2 V^{-1} s^{-1}$)	Туре
B-N codoped	2.3	1.2E+17	11	р
N-doped film	5.0E+1	3.6E+16	4.4	р



Figure 3. (Color online) I-V characteristics of the homojunction composed of undoped n-type ZnO and B–N codoped p-type ZnO. The upper left inset shows a schematic structure of the p–n heterojunction. The lower right inset shows the Ohmic contact characteristic of two Ni/Au contacts on p-type and two In contacts on n-type ZnO.

is that H escapes from ZnO [21]. Table 1 gives the electrical properties of the B-N codoped and N-doped p-type ZnO films obtained by annealing of 923 K. The room-temperature resistivity was found to be $2.3 \,\Omega \,\text{cm}$ with a Hall mobility of $11 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ and a carrier concentration of $1.2 \times 10^{17} \text{ cm}^{-3}$ for the B-N codoped p-type ZnO film. In order to verify further p-type conduction, an I-V characteristic of a ZnO homojunction synthesized by deposition of the undoped n-ZnO layer on the B-N codoped p-ZnO layer was investigated and is shown in figure 3. The schematic structure of the ZnO p-n homojunction is shown in the upper left inset. Indium electrodes were used to form Ohmic contacts to the n-type layer and Ni/Au electrodes were used to form Ohmic contacts to the p-type layer as reported in the literature [22, 23]. In order to obtain good Ohmic contacts between the ZnO films and the electrodes, the contacts were annealed rapidly at 673 K for 3 min and 5 min, respectively. As shown in the lower right inset, the linear behaviour of I-V curves measured from both Ni/Au on p-type and In on n-type demonstrates the Ohmic nature of the contacts. This indicates that a rectifying behaviour was achieved, as suggested by the data shown in figure 3, which can be considered as proof of p-type behaviour achieved in the set of films developed along this work. It is found from table 1 that the p-type characteristics of B-N

codoped ZnO are better than that of N-doped ZnO. A similar result is also obtained in the comparison of electrical properties between codoped ZnO, such as Ga-N, Al-N and In-N, and N-doped ZnO [11, 14, 16]. It is usually attributed to that the N concentration incorporated into ZnO is higher in III-V codoping than in N-doping, based on first principle calculation results [8–10]. B is a group-IIIB element like Al, Ga and In and can make the formation energy of ZnO decrease as doped in ZnO, leading to incorporation of more group-VB elements (such as N) into ZnO when it codopes with a group-VB element [9]. Unlike Al and Ga, which have a similar atomic radius to Zn, the atomic radius of B is much smaller than that of Zn, the large difference in the atomic radius will produce considerable lattice distortion, resulting in the production of elastic energy and increment in the formation energy. Therefore, Al-N and Ga-N are considered as good candidates for III-V codoping and have been investigated widely in recent years [11–16], while B-N codoping is not seriously considered. However, the B-N codoped ZnO film with acceptable p-type behaviour was successfully obtained in this work and p-type characteristics were improved remarkably for the B-N codoped ZnO film as compared with the N-doped ZnO film, demonstrating that B-N is also a good candidate for III-V codoping.

In addition to the fabrication of p-type ZnO, the time stability of p-type ZnO is also an important issue. Barnes et al have noted that p-type ZnO films revert to n-type in time after deposition [24]. Hydrogen-generated donors were suggested to explain the observed electrical behaviour. Wang and Zunger have also observed a similar phenomenon and attribute it to a metastable N-on-O substitution, which serves as donors [7]. Some reports showed that p-type conductivity seems to be unstable and it can even convert to n-type conductivity after exposure to light [25]. In our present work, we also found that conductivity of B-N codoped ZnO changed from p- to n-type after a period of time. For some samples, it takes a few days, but for some samples, it takes several weeks. We now take up the investigation of the stability of B-N codoped p-type ZnO conductivity, but do not understand the nature of this erratic p-type conductive behaviour now. Therefore, the stability of B-N codoped p-type ZnO conductivity will be studied in detail in our subsequent work.

Figure 4 shows the temperature-dependent PL spectra of the N-doped p-type ZnO film, the 83 K PL spectrum of which exhibits clearly resolved emission at 3.363, 3.327, 3.255 and 3.183 eV. The peak at 3.363 eV can be assigned to a neutral donor bound exciton (D^0X) having a donor binding energy of 56 meV [26]. The emission peak at 3.327 eV can be attributed to the conduction band to acceptor transition (or free electrons to the acceptor (FA) transition) as reported in arsenicdoped ZnO [27]. Accompanying the FA, two step-like broad peaks appear at 3.255 and 3.183 eV with a periodic spacing of ~72 meV, respectively. Since this energy difference is almost identical to the longitudinal optical (LO) phonon energy, the step-like broad peaks are assigned to LO phonon replicas of FA-nLO (n = 1, 2) [28].

Differing from the 83 K PL spectrum of the N-doped ZnO, the 83 K PL spectrum of the B–N codoped ZnO shows two dominant peaks, located at 3.096 eV and 3.251 eV,



Figure 4. (Color online) PL spectra of the N-doped ZnO film measured at temperatures from 83 to 300 K.



Figure 5. (Color online) PL spectra of the B–N codoped ZnO film measured at temperatures from 83 to 300 K. The inset shows the 83 K PL spectra of the B–N codoped ZnO film prepared by using a mixture of (*a*) Ar and N₂ and (*b*) Ar and O₂.

respectively, as shown in figure 5. The 3.251 eV peak is often observed in N-doped ZnO with good p-type conductivity and assigned to the emission of a native donor and an N-related acceptor pair (DAP). The N-related acceptor is formed by substitutional N for O in ZnO (denoted as N_O). In our other work, it was found that the peak located at about 3.096 eV is also observed in the low-temperature PL spectrum of B–N codoped ZnO prepared by using a mixture of Ar and N₂, but not in the low-temperature PL spectrum of B–N codoped

ZnO prepared by using a mixture of Ar and O_2 , as shown in the inset. Furthermore, the position of the peak is in the range between 3.096 and 3.170 eV. These results indicate that the appearance of the dominant 3.096 eV is related to incorporation of more N atoms into ZnO. In fact, this peak is also found in the low-temperature PL spectrum of Al-N and Ga–N codoped ZnO and is a dominant emission peak [14, 29]. It is attributed to recombination of the Al (or Ga) donor and N acceptor pair. However, 3.096 eV is also close to the value of radiative electron transition from the conduction band to the V_{7n} acceptor level [30]; moreover, this peak is also found in the 83 K PL spectrum of undoped p-type ZnO obtained by annealing at 1073 K. It is known that p-type conductivity of the undoped ZnO is due to contribution of V_{Zn} . Therefore, we deduce that the emission peak located near 3.096 eV comes from radiative electron transition from the conduction band to the V_{Zn} acceptor level. Since N atoms occupy the O site in ZnO, incorporation of more N atoms into ZnO will result in the formation of anion-rich ZnO with a lot of V_{Zn} . It can be seen from figure 5 that the intensity of the 3.096 eV peak decreases with the increase in temperature, implying that V_{Zn} is ionized and the number of ionized V_{Zn} increases with the increase in temperature, which induces increment in the numbers of hole. Therefore, p-type conduction of B-N codoped ZnO comes from the contribution of V_{Zn} and N_O acceptors.

4. Conclusion

In summary, we have presented a method to realize a p-type ZnO film with good electrical and luminescent properties by codoping of boron and nitrogen using rf magnetron sputtering. The Hall measurement indicates that the roomtemperature resistivity was found to be 2.3Ω cm with a Hall mobility of $11 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ and a carrier concentration of $1.2 \times 10^{17} \,\mathrm{cm}^{-3}$ for the B-N codoped p-type ZnO thin film on quartz substrate. The p-type characteristics were improved remarkably as compared with N-doped ZnO films. A ZnO homojunction was prepared by depositing an ntype ZnO layer on the B-N codoped p-type ZnO film and showed rectification behaviour. Differing from N-doped ZnO, the low-temperature PL spectrum consists of two dominant peaks located at 3.096 eV and 3.251 eV, respectively. The 3.096 eV peak comes from radiative electron transition from the conduction band to the V_{Zn} acceptor level and the 3.251 eV peak from recombination of DAP. The p-type conductivity is attributed to contribution of V_{Zn} and N_O acceptors.

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