Li–N dual-doped ZnO thin films prepared by an ion beam enhanced deposition method

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Li–N dual-doped ZnO films [ZnO:(Li,N)] with Li doping concentrations of 3 at.%–5 at.% were grown on a glass substrate using an ion beam enhanced deposition (IBED) method. An optimal p-type ZnO:(Li,N) film with the resistivity of 11.4 Ω·cm was obtained by doping 4 at.% of Li and 5 sccm flow ratio of N_2. The ZnO:(Li,N) films exhibited a wurtzite structure and good transmittance in the visible region. The p-type conductive mechanism of ZnO:(Li,N) films are attributed to the Li substitute Zn site (Li_{Zn}) acceptor. N doping in ZnO can forms the Li_i–N_O complex, which depresses the compensation of Li occupy interstitial site (Li_i) donors for Li_{Zn} acceptor and helps to achieve p-type ZnO:(Li,N) films. Room temperature photoluminescence measurements indicate that the UV peak (381 nm) is due to the shallow acceptors Li_{Zn} in the p-type ZnO:(Li,N) films. The band gap of the ZnO:(Li,N) films has a red-shift after p-type doping.

Keywords: ZnO, ion beam enhanced deposition, photoluminescence

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1. Introduction

ZnO is a direct wide-band-gap (3.37 eV) semiconductor with an exciton binding energy of 60 meV, which makes it a promising material for a number of applications, such as high-temperature electronics, transparent electronics, and blue to UV optoelectronics. In order to realize the potential applications of ZnO, high quality n-type and p-type ZnO films are necessary. Currently, n-type ZnO films can be prepared easily, whereas it is very difficult to obtain stable and reproducible p-type ZnO due to the high ionization energy of acceptor impurities, the low solubility of dopants, and the self-compensation effect in ZnO.[1,2] P-type ZnO may be achieved by the substitution of group-I elements on the Zn-site[3–5] and group-V elements on the O-site,[6–9] respectively. It has been shown that choosing appropriate acceptor dopants and doping methods is very important for the preparation of p-type ZnO. In recent years, great efforts have been made to obtain p-type ZnO by doping groups I and V elements. Li and N are regarded as the best dopants due to the matching of their atomic radius with Zn and O, and to their shallow acceptor levels.[10,11] Theoretical calculations have predicted that Li prefers to occupy interstitial sites (Li_i), acting as the donor, rather than the Zn sites (Li_{Zn}), acting as the acceptor.[12] They have also shown that there is very low N solubility at O sites (N_O) in ZnO crystals, and there is a possibility of N_2 occupying O sites $(N_2)_O$, acting as shallow double donors.[13,14] Lee *et al.* investigated possible p-type doping with group-I elements in ZnO. They found that Li and Na are better acceptors with shallower acceptor levels than N, while they are mostly self-compensated by Li and Na interstitials, respectively.[15] A co-doping method of Li and N is used to fabricate p-type ZnO films, expecting to depress the compensation of Li_i donor for Li_{Zn} acceptor,[16–18] while increasing N solubility in ZnO. Lu *et al.* prepared p-type ZnO thin films using pulsed laser deposition (PLD).[19] They observed much lower resistivity for Li–N co-doped ZnO thin films than that of Li or N-monodoped ZnO films. Although there are several reports on the preparation of stable p-type ZnO films by using Li and N as dopants,[20–23] the formation mechanism of the p-type conduction is still unclear and, hence, a comprehensive investigation of the fundamental properties of acceptors in ZnO is necessary. In this paper we used the ion beam enhanced deposition method (IBED) to prepare Li–N co-doped ZnO (denoted as ZnO:(Li,N)) films and investigated the p-type conductive mechanism of ZnO:(Li,N) films. As a comparison, we also prepared Li monodoped ZnO (denoted as ZnO:Li) films and compared the effects of different Li and N doping concentrations on the electrical, structural, and optical properties of ZnO:(Li,N) films.

2. Experiment

ZnO targets were made up of ZnO (99.9% in purity) powder, which was mixed with different weights of Li_2O (99.9% in purity) powder. Before deposition, the glass substrates were thoroughly cleaned with acetone, isopropanol, deionized water, and finally cleaned with the help of an ultrasonic bath for 30 min, they were then nitrogen dried. Subsequently, the Li-doped ZnO ceramic target was sputtered by Ar^+ ions with energy of 2.5 keV. The direction of sputtering beam was 45° with respect to the target. The substrates were placed on a round holder rotated with a speed of 24 rpm.[24] After being deposited for half an hour, a different flow ratio N^+ ion beam,

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which was extracted from the ion source with an energy of 20 keV and a beam current of 2 mA, was vertically implanted into the deposited ZnO films; Li and N were co-doped into ZnO simultaneously. All of the films were deposited for 2 h and the thickness of the films was about 200 nm. After deposition, the films were annealed under different conditions. The annealing treatments were performed in a rapid thermal annealing (RTA) oven. X-ray diffraction (XRD) with Cu $K_{\alpha 1}$ radiation ($\lambda = 0.1541$ nm) was used to evaluate the phase characteristics of the samples. The surface morphologies of the ZnO thin films were analyzed by scanning electron microscopy (SEM). A SDY-4 four-point probe system was used to determine the conductive type and resistivity of the samples. The optical transition through the film was measured by a UV-2450 UV–visible spectrophotometer. Room temperature photoluminescence (PL) spectra were recorded in the range of 300–700 nm by a spectrophotometer. The 325-nm laser line from helium–cadmium laser was employed as an excitation source for the PL measurement.

3. Results and discussion

ZnO:(Li,N) films were annealed at different temperatures in Ar, N_2, O_2 atmosphere for various annealing times. We found that the p-type conductive properties of ZnO:(Li,N) films were better in Ar than in N_2 and O_2, and better annecled at 500 °C than at other temperatures. Hence, we mainly studied the properties of ZnO:(Li,N) films annealed at 500 °C in Ar.

3.1. XRD analysis

Figure 1 shows the XRD patterns of the ZnO:(Li,N) films with different Li doping concentrations. There are three prominent peaks, which correspond to (100), (002), and (101) planes of the ZnO crystal. The positions and relative intensities of the three dominant peaks match well with the standard XRD pattern of bulk zinc oxide (JCPDS PDF card No:79-2205).[25] There are no other peaks related to Li_3N, Li_2O, Zn_3N_2, or other mixed compounds. All of the ZnO:(Li,N) films possess a hexagonal wurtzite structure. The XRD spectra do not show any evident change with different Li doping concentrations. This indicates that ZnO:(Li,N) films could be prepared in a wide range of Li doping concentrations.

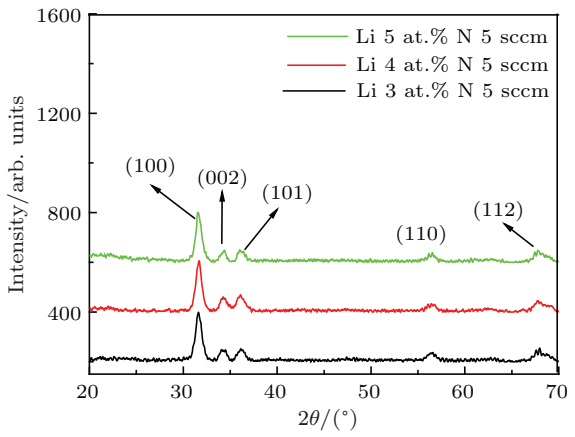


Fig. 1. XRD patterns of ZnO:(Li,N) films annealed at 500 °C in Ar for 30 min.

3.2. SEM analysis of ZnO:(Li,N) films

Figure 2 shows SEM images of ZnO:(Li,N) films with doping concentrations of 4 at.% of Li and 5 sccm flow ratio of N_2 and annealed at 500 °C in Ar for 30 min. The scanning area was 5 μm×5 μm. We can see from Fig. 2(a) that the ZnO atoms have been crystallized to a certain extent during deposition because ion sputtering and implanting generated enormous amounts of thermal energy. The morphology of the annealed sample is displayed in Fig. 2(b). We can see that the grain sizes of the annealed sample become larger than that of the unannealed sample. Larger grain sizes indicate a better crystal quality. This indicates that the quality of ZnO:(Li,N) films can be enhanced by annealing.

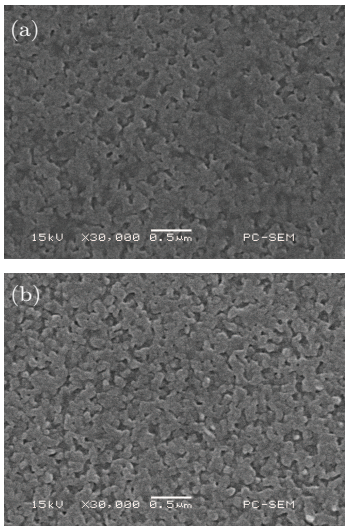


Fig. 2. Morphologies of ZnO:(Li,N) thin films: (a) unannealed and (b) annealed.

3.3. Electrical properties

In order to study the effects of N doping concentration on the electrical properties of ZnO:(Li,N) films, N^+ ion beams with 0 sccm, 1 sccm, 5 sccm, and 10 sccm flow ratios of N_2 gas were implanted into Li-monodoped ZnO (denoted as ZnO:Li) films, respectively. The electrical properties of ZnO;Li and ZnO:(Li,N) films with different Li doping concentrations are listed in Table 1. All of the films showed n-type conduction, except for the film implanted by 5 sccm flow ratio of N_2. The action of N^+ ions in ZnO:(Li,N) films can be seen from Table 1. All of the ZnO;Li films with different Li doping concentrations show n-type conduction. This indicates that there are few Li_{Zn} atoms in ZnO:(Li,N) films and that Li atoms prefer to form Li_i donors, which combine with few Li_{Zn} atoms to

form Li_i–Li_{Zn} neutral impurities rather than Li_{Zn} acceptors in ZnO crystals, resulting in the n-type conduction. This result is in agreement with that in Refs. [23] and [24]. The ZnO:(Li,N) films also show n-type conduction when an N^+ ion beam with 1 sccm flow ratio is implanted into Li-monodoped ZnO films, indicating that the number of N^+ ions was too few to compensate with excessive Li_i atoms in ZnO films and that the number of Li_i atoms was larger than that of Li_{Zn} atoms in the films. However, when a N^+ion beam with 5 sccm flow ratio is implanted into Li-monodoped ZnO films, the conductive type of ZnO:(Li,N) films changed from n-type conduction to p-type conduction. This indicates that N^+ ions can help to carry out p-type conduction of ZnO:(Li,N) films when the number of N^+ ions are large enough to compensate with superfluous Li_i atoms and form a Li_i–N_O complex. The Li_i–N_O complex is dielectric, which cannot provide electrons or holes in ZnO:(Li,N) films but may affect the electrical properties of ZnO. This depresses the compensation of Li_i for Li_{Zn},[26] and makes the number of Li_{Zn} atoms increase. However, when the N flow ratio was excessive, for example reaching 10 sccm, the films again show n-type conduction. This demonstrates that excessive N doping will form $(N_2)_O$, acting as shallow double donors. This will compensate for the hole carriers (the Li_{Zn}) resulting in the disappearance of p-type conduction.[13]

Table 1. Electrical properties of ZnO;Li and ZnO:(Li,N) films annealed at 500 °C in Ar for 30 min.

Li concentration /at.%	N_2 gas flow /sccm	Carriers type	Resistivity /(Ω·cm)
3.0	0	n	1.40
3.0	1	n	55.9
3.0	5	p	200
3.0	10	n	40
4.0	0	n	1.1
4.0	1	n	14.5
4.0	5	p	11.4
4.0	10	n	35.1
5.0	0	n	0.8
5.0	1	n	11.2
5.0	5	p	56
5.0	10	n	31.1

For the effects of Li doping concentration on the electrical of ZnO:(Li,N) films, it can been seen that the resistivity of n-type ZnO:Li and ZnO:(Li,N) films decreases as the Li doping concentration increases, relating to the same N concentration. This indicates that the electron concentration became larger when N was implanted into the films and hinted that the N combined with Li_i to form a Li_i–N_O complex. Meanwhile, p-type ZnO:(Li,N) films showed the lowest resistivity of 11.4 Ω·cm at 4 at.% of Li doping. When Li doping concentration increases from 3 at.% to 5 at.%, relating to 5 sccm N_2 gas flow ratio, the resistivity of ZnO:(Li,N) film first decreases from 200.0 Ω·cm to 11.4 Ω·cm and then increases to 56.0 Ω·cm. This reveals that the hole concentration or Li_{Zn} atoms increased as the Li doping concentration increased from 3 at.% to 4 at.% but decreased as the Li doping concentration increased from 4 at.% to 5 at.%. This indicates that some Li_i may not combine with N_O to form a Li_i–N_O complex due to the limited solubility of N_O in ZnO, which leads to the existence of excessive Li_i. The excessive Li_i will compensate for the Li_{Zn} acceptor, resulting in the resistivity increase of p-type ZnO:(Li,N) films.

3.4. PL measurements

It is well known that there are three PL peaks for intrinsic ZnO. They are the near-band-edge (NBE) ultraviolet (UV) emission at about 380 nm, the green emission at about 510 nm, and the red emission at about 650 nm.[27] Figure 3 shows the PL spectra of ZnO:(Li,N) films with the same Li doping concentration (4 at.%) and different N doping concentrations at room temperature. All of the PL spectra of the ZnO:Li and ZnO:(Li,N) films show a strong peak in the UV region at 381 nm, and two weak (deep-level emission) peaks in the visible region at 490 nm and 580 nm. This indicates that the UV peak (at 381 nm) is due to the shallow acceptors Li_{Zn}.[22,23] The emission intensity of the UV peak (at 381 nm) increases with the increase of N doping concentration from 0 to 5 sccm flow ratio. This indicates that N_O is easily combined with Li_i to form a Li_i–N_O complex so as to depress the compensation of Li_i donors for Li_{Zn} acceptors, The stronger the UV peak (at 381 nm) is, the more Li_{Zn} atoms there are. The Li_i–N_O complex has neutral impurities: it produces non-radioactive recombination centers that cannot be seen in the PL measurements.[20] Figure 4 shows the PL spectra of ZnO:(Li,N) films with different Li doping concentrations and the same N doping concentration at room temperature. The peak position is similar to that in Fig. 3. It can be seen from Fig. 4 that the emission intensity of the UV peak increases with the increase of Li doping concentration from 3 at.% to 4 at.% but decreases with the increase of Li doping concentration from 4 at.% to 5 at.%. When the Li doping concentration is 3 at.%, the lower height of the UV peak corresponds the fewer Li_{Zn} acceptors. When Li doping concentration is higher than 4 at.%, excessive Li_i donors compensate for the Li_{Zn} acceptors, resulting in the decrease of emission intensity of the UV peak. The intensity change of the UV peak is consistent with the resistivity change of the p-type ZnO:(Li,N) films analyzed in Section 3.3. The intensity of the deep-level emission in the vicinity of yellow–green region is much lower than that of the UV peak. This indicates that Li and N doping can reduce oxygen vacancies in a ZnO lattice.[21] The PL spectra of the ZnO:Li and ZnO:(Li,N) films show an obvious red-shift (about 10 nm shown in Fig. 5) in the UV emission in comparison to that

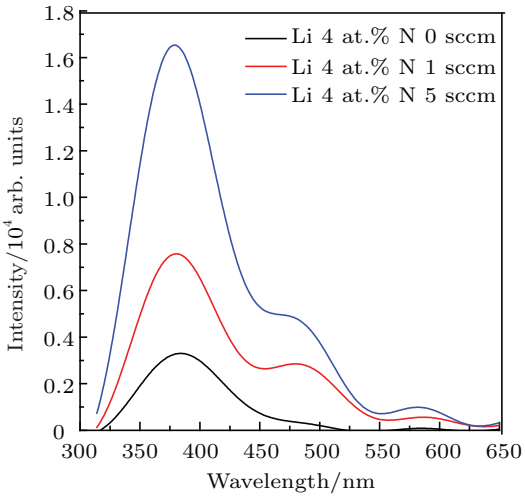


Fig. 3. Room temperature PL spectra of ZnO:(Li,N) films with the same 4 at.%. of Li and different N doping concentrations annealed at 500 °C in Ar for 30 min.

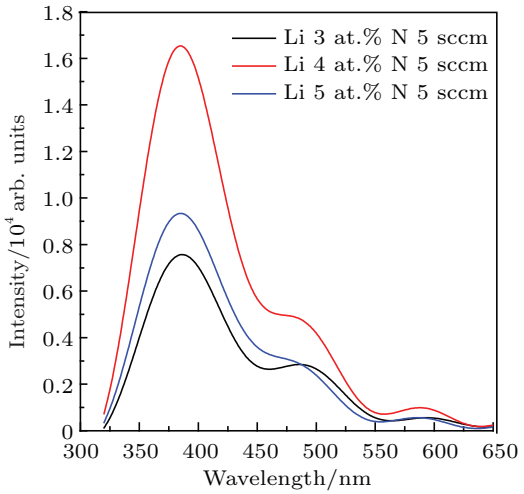


Fig. 4. Room temperature PL spectra of ZnO:(Li,N) films with the same N content and different Li doping concentrations annealed at 500 °C in Ar for 30 min.

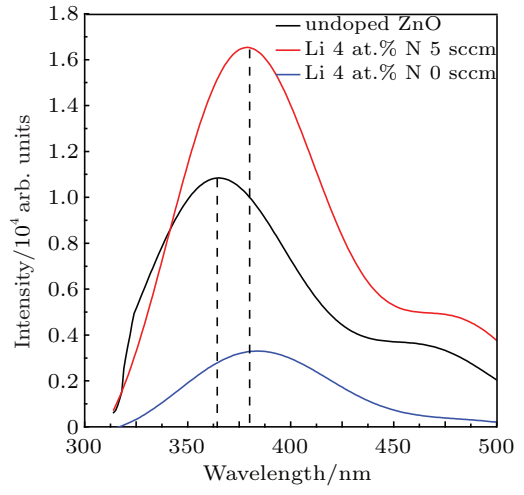


Fig. 5. Room temperature PL spectra of ZnO:(Li,N), ZnO:Li, and undoped ZnO films annealed at 500 °C in Ar for 30 min.

observed for the undoped ZnO. This result is the same as Ramin Yousefi's result.[28] This red-shift in the UV emission could be used to obtain p-type ZnO. In fact, the UV peak of the PL spectra of the ZnO films doped by donor materials exhibit a blue-shift in comparison to that observed in undoped ZnO nanostructures.[29,30]

3.5. Optical properties

The optical transmittance spectra of p-type ZnO:(Li,N) films are given in Fig. 6. The visible light transmittance is above 70%. The visible light transmittance of ZnO:(Li,N) films increases as the Li doping concentration goes up. Meanwhile, the absorption edge of ZnO:(Li,N) films has a red-shift with the increase of Li doping concentration. The band gaps of the ZnO:(Li,N) films are estimated by optical absorption spectra. Figure 7 shows the $(\alpha h\upsilon)^2$ of the ZnO:(Li,N) with various Li doping concentrations as a function of the photon energy, where α is the absorption coefficient and $h\nu$ is the photon energy. For direct band gap semiconductors, the relationship between α and energy gap E_g can be written as

$$(\alpha h\nu)^2 = A(h\nu - E_g), \tag{1}$$

where the coefficient A is a parameter related to the band tail states and E_g is energy gap. Using the data in Fig. 7 and Eq. (1), the band gaps of ZnO:(Li,N) with Li doping concentrations of 3 at.%, 4 at.%, and 5 at.% were evaluated to be 3.35 eV, 3.30 eV, and 3.28 eV, respectively, all of which are smaller than that of intrinsic ZnO. The band gap usually becomes wide for ZnO doped with donors, while p-type ZnO shows a band gap reduction if doped with acceptors. According to the previous discussion, the band gap narrowing of p-type ZnO may be ascribed to the following effects: (i) the formation of the Li_i–N_O complex generates an additional fully occupied impurity band above the valance band maximum (VBM), resulting in an upward shift of the VBM and a decrease in the band gap;[10,20]

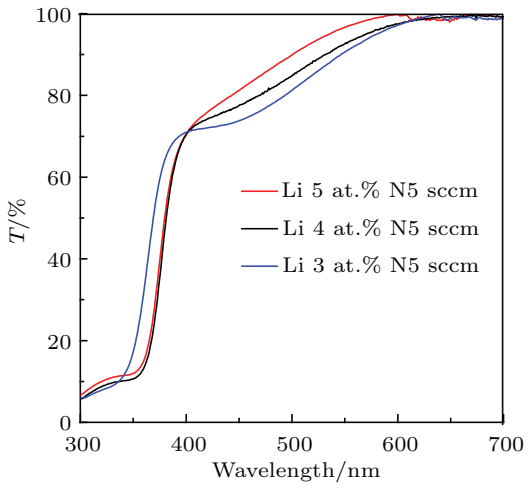


Fig. 6. Optical transmittance spectra of ZnO:(Li,N) films with the same N doping concentration and different Li doping concentrations annealed at 500°C in Ar for 30 min.

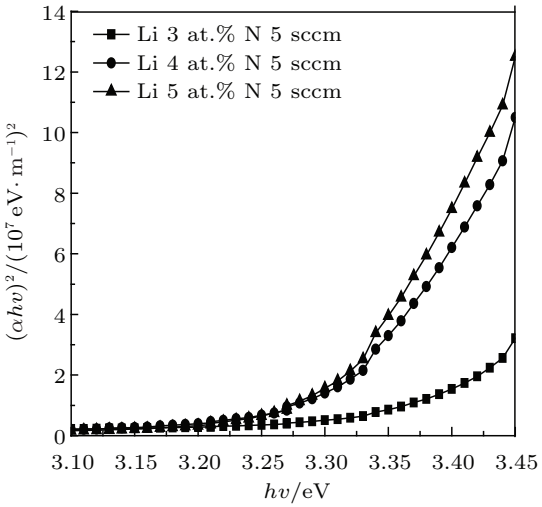


Fig. 7. $(\alpha h\upsilon)^2$ versus $h\nu$ spectra of ZnO:(Li,N) films with the same N doping concentration and different Li doping concentrations annealed at 500 °C in Ar for 30 min.

and, (ii) Li and N atoms are doped into the ZnO matrix, leading to the formation of more and more Li–O and Zn–N bonds. The lengths of Li–O (0.197 nm) and Zn–N (0.196 nm) bonds were slightly shorter than that of Zn–O (0.199 nm) bond, which could make the lattice constant decrease and produce some strain in the films. The strain changes the inter atomic spacing of the semiconductors, which affects the energy gap.[24,25]

4. Conclusion

Li–N dual-doped ZnO films with p-type conduction have been obtained by IBED method and rapid annealing at 500 °C in Ar for 30 min. The main conductive mechanism of p-type ZnO:(Li,N) thin films is Li_{Zn}, according to the electrical and optical analysis. The N doping in ZnO films can form a Li_i–N_O complex, which depresses the compensation of Li_i donors for Li_{Zn} acceptors and which helps to achieve p-type conduction of ZnO:(Li,N) films. The shortage and excess of Li and N in ZnO films goes against the p-type conduction. The suitable Li doping concentration is 4 at.% and the suitable N doping concentration is a 5 sccm flow ratio. In this doping condition, the ZnO:(Li,N) films have the lowest resistivity of 11.4 Ω·cm and exhibit a p-type conduction. The Li_{Zn} emission peak is the strongest observed at 381 nm at room temperature, which is found by using PL measurements. The band gap of ZnO:(Li,N) films has a red-shift after p-type doping.

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