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Acceptor formation mechanisms determination from electrical and optical properties of p-type ZnO doped with lithium and nitrogen

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Abstract

A lithium (Li) and nitrogen (N) dual-doped p-type ZnO film (ZnO : (Li,N)) was deposited on c-plane sapphire by RF-magnetron sputtering of Zn–2 at.% Li alloy using mixed gases of oxygen and nitrogen and then annealing in N_2 flow. It has a carrier concentration of $3.07 \times 10^{16}\,\mathrm{cm^{-3}}$ and Hall mobility of $1.74\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. XPS measurement shows that there are Li_{Zn}–N complexes in the p-type ZnO : (Li,N), which are demonstrated by photoluminescence measured at various temperatures and different excitation powers to be acceptors and responsible for p-type conductivity of the ZnO : (Li,N). The optical level of the Li_{Zn}–N complex acceptor is estimated to be about 126 meV by measurement of emission energy of free electron to the acceptor level.

1. Introduction

Wurtzite ZnO is a II-VI compound semiconductor with 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, a tunable gap mixed with Cd and Mg between 3.0 and 4.0 eV and so on. These properties make ZnO a promising material for use in ultraviolet light-emitting diodes, laser diodes and photodetectors [1]. In order to realize ZnO-based devices, it is necessary to prepare both high-quality n- and p-type ZnO films. The high-quality n-type ZnO can be easily achieved by doping with Al, Ga or In [2], but fabrication of p-type ZnO is still a major problem. The realization of p-type ZnO can be doped by group-V elements (such as N, P, As) substituting for O or group-I elements (such as Li, Na) substituting for Zn. There are several reports on the growth of p-type ZnO by doping with N [3–5], P [6–9], As [10–12] and Sb [13]. Theoretically, Li substitutes for Zn(Li_{Zn}) possess shallower acceptor level [14]. However, the ZnO doped by Li usually is a semi-insulator [15] that is attributed to the formation of donor complex, such as interstitial Li atom (Li_i) and Li_{Zn}–Li_i complex [16]. So, it is important to repress formation of Li_i for realization of Li doped p-type ZnO. An effective method of repression of Li_i may be by co-doping with Li and a dopant, which can bond with Li to form an acceptor complex with shallow level. We have obtained p-type ZnO by doping Li and N (ZnO : (Li,N)) [17]. Recently, p-type ZnO : (Li, N) doping was also realized by Ye *et al* [18]. However, the formation mechanism of the p-type ZnO : (Li,N) is unclear yet.

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In the present work, the Li and N dual-doped p-type ZnO was successfully fabricated by RF-magnetron sputtering method and post annealing technology, and the electrical and optical properties as well as formation mechanism of the p-type ZnO : (Li,N) were investigated.

2. Experiments

A Zn–Li alloy with nominally 2 at.% Li was prepared by the arc-melting technique. X-ray diffraction (XRD) confirmed that Li incorporated into ZnO by substituting for Zn, and the Li content was estimated to be about 1.63 at.% by using the XRD data and Vegard formula. A 500 nm thick Li and N doped ZnO film with wurtzite structure (denoted as ZnO : (Li,N)) was grown on a c-plane Al_2O_3 substrate at 300 K by RF-magnetron sputtering the Zn–Li alloy. A mixed gas of oxygen and nitrogen with a ratio of 1 : 1 was used as the sputtering gas with a total pressure of 1.0 Pa. Before deposition, the substrate was treated with ethanol in an ultrasonic bath to remove surface contaminations and etched in a hot (160 °C) $H_2SO_4 : H_3PO_4$ (3 : 1) solution for 10 min and then rinsed in de-ionized water (18.2 MΩ cm) and blown dry using high-purity nitrogen. The as-grown films were annealed in a N_2 flow at 500 °C, 600 °C and 700 °C respectively. XRD measurement was performed by using a Rigaku O/max-RA x-ray diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.154\,18$ nm). The electrical properties were investigated by Hall measurement in the Van der Pauw configuration at room temperature using a current of 300 nA and magnetic fields of 3000–180 00 G (Lakershore HMS 7707). Electrodes were fabricated by depositing metal indium on the surface of films and sintering at a pressure of $\leqslant 10^{-5}$ Torr. Ohmic contact between the indium spots and film was confirmed prior to Hall measurement. The photoluminescence (PL) of the films was measured in a temperature ranging from 80 to 176 K by using 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. Results and discussion

Figure 1(*a*)–(*d*) show XRD patterns of the as-grown film and annealed at 500 °C, 600 °C and 700 °C respectively. The as-grown film only exhibits a weak and broad (002) diffraction peak, indicating that the film is preferential oriented in (002) direction and has poor crystal quality. After annealing, the (002) peak becomes strong and sharp, and the diffraction angle shifts towards a higher angle but changes little in the annealing temperatures between 500 and 700 °C, as shown in figure 1. The former implies improvement of crystal quality of the film, and the latter is due to relaxation of tensile stress in the film [19]. The lattice constant *c* is calculated to be 0.519 7 nm for the film annealed at 600°C, which is somewhat smaller than the value of 0.520 7 nm of bulk ZnO [20]. Since Zn–O and Li–N covalence bond lengths are 0.199 nm and 0.197 nm, respectively, the fact that the lattice constant of the 600 °C-annealed film is smaller than that of bulk ZnO implies that Li and N may incorporate into ZnO in a form of a Li–N pair or cluster.

In order to investigate the chemical states of lithium and nitrogen in the ZnO : (Li,N) film, x-ray photoelectron spectrum (XPS) of the ZnO : (Li,N) film annealed at 600 °C was measured using an Al K_α x-ray source, as illustrated in figure 2. The film was sputtered by Ar^+ for 16 min prior to XPS measurement to remove the surface contaminations. As figure 2 shows, three N_{1S} peaks were observed at 396.1 eV, 399.1 eV and 403.7 eV, respectively, and a Li_{1s} peak was at 56.15 eV. The 399.1 eV peak is dominant among the three N_{1S} peaks, its binding energy is close to the binding energy of C–N bonds and Li–N in lithium azide of Li(N*NN*) [21]. Since no C element is doped in the ZnO : (Li, N) and no C_{1s} peak related to the C–N bond was detected by XPS, the peak at 399.1 eV should not be due to radiation from N_{1s} in the C–N bond but from the Li–N bond similar to Li–N in lithium azide. The 56.15 eV is found to be close to the binding energy of Li of 55.6 eV in the Li–O bond [22] and the binding energy of 55.2 eV in the Li–N bound in lithium azide, so that the Li may bond with O and N. According to figure 2, the atomic ratio of Li to N (related to the 399.1 eV peak) is estimated to be about 1 : 2. Based on the above discussion, it is deduced that Li and

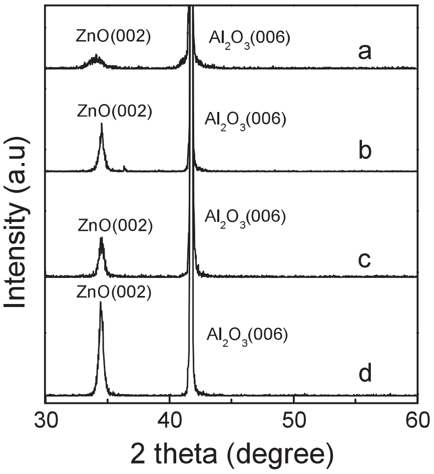

Figure 1. XRD patterns of as-grown ZnO : (Li,N) (a) and annealed at 500 °C (b), 600 °C (c) and 700 °C (d), respectively.

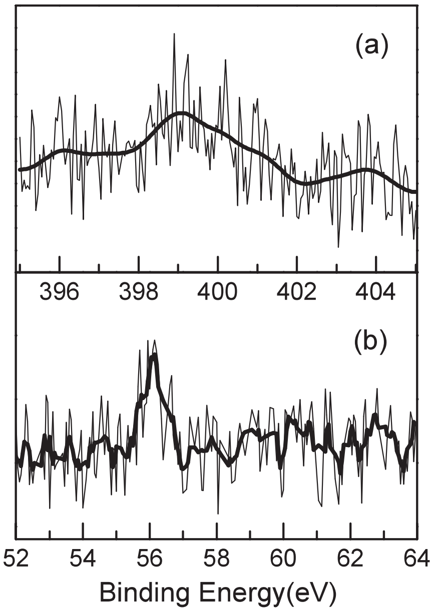

Figure 2. XPS spectra of N_{1s} (*a*) and Li_{1s} (*b*) of the p-type ZnO : (Li,N) annealed at 600 °C.

Table 1. Electrical properties of as-grown ZnO : (Li,N) and annealed at various temperatures.

Growth conditions	Type	Resistivity (Ω cm)	Mobility (cm^2 V^{-1} s^{-1})	Carrier concentration (cm^{-3})
As-grown		High		
500°C	p/n	$1.748\,4 \times 10^{3}$	0.5414	$6.732\,7 \times 10^{15}$
600°C	p	$1.190\,5 \times 10^{2}$	1.743 8	$3.076\,4 \times 10^{16}$
700°C	p/n	$1.381\,1 \times 10^{2}$	1.895 1	$2.584\,8 \times 10^{16}$

N incorporate mainly into ZnO in a form of a Li–N complex: one Li substitutes for Zn sublattice (denoted as $\mathrm{Li_{Zn}}$) and two N substitute for O sites (denoted as $\mathrm{N_O}$), respectively. The $\mathrm{Li_{Zn}}$ bonds with the $\mathrm{N_o}$ and O to form a $\mathrm{Li_{Zn}}$–$\mathrm{N_2O_2}$ cluster, which is a predominant defect resulted from Li and N doping. The peaks at 403.7 eV and 396.1 eV are due to $\mathrm{(N_2)_o}$ and $\mathrm{(N)_o}$, defects, respectively, [23]: the $\mathrm{(N_2)_o}$ represents substitution of $\mathrm{N_2}$ for O sublattice and the $\mathrm{(N)_o}$ represents substitution of N atom for O site. The $\mathrm{(N_2)_o}$ is a double donor, and the $\mathrm{(N)_o}$ is an acceptor.

Electrical properties of both as-grown and annealed ZnO : (Li,N) films were measured by Hall measurement, as listed in table 1. The as–grown film behaves as an insulator. The film annealed at 600 °C shows stable p-type conductivity, while the films annealed at 500 and 700 °C show weak p-type conduction, showing alternanting appearance of p- and n-type conduction in the Hall measurement process. It is found from figure 2 (*b*) that the area of $\mathrm{N_{1s}}$ of $\mathrm{(N)_o}$ acceptor is about two times that of $\mathrm{(N_2)_o}$ double donors, so the holes generated from $\mathrm{(N)_o}$ should be compensated by electrons coming from the $\mathrm{(N_2)_o}$ and the p-type conduction of the ZnO : (Li,N) does not come from the contribution of $\mathrm{(N)_o}$. Since $\mathrm{Li_{Zn}}$ and $\mathrm{(N)_o}$ are acceptors, it is deduced reasonably that the Li–N complex is an acceptor cluster and that p-type conductivity of the ZnO : (Li,N) comes mainly from the contribution of the Li–N complex acceptors.

It is well known that there are $\mathrm{V_O}$ and $\mathrm{Zn_i^1}$ donors defect in ZnO, which produce PL bands in visible light range [24]. The present room-temperature PL measurement shows that intensity ratio of visible band to ultraviolet band for the ZnO : (Li,N) annealed at 600 °C is much smaller than that of the ZnO : (Li,N) annealed at 500 and 700 °C, as shown in figure 3, implying that the amount of $\mathrm{V_O}$ or $\mathrm{Zn_i}$ in the ZnO : (Li,N) annealed at 600 °C is much smaller than that of the ZnO : (Li,N) annealed at 500 and 700 °C. Therefore, the difference in stability of p-type conductivity between the ZnO : (Li,N) annealed at 600 °C and 500 and 700 °C is due to that they have different amounts of $\mathrm{V_O}$ and $\mathrm{Zn_i}$ defects.

The low-temperature (80 K) PL measurements were conducted to characterize optical properties of ZnO : (Li,N) films annealed at 500, 600 and 700 °C, as shown in figure 4. For the ZnO : (Li,N) annealed at 500 °, the PL spectra is very broad ,and the peak cannot be distinguished clearly, as shown in panel (*a*) of figure 4. For the ZnO : (Li,N) annealed at 700 °C, one dominant peak at 3.310 eV is ascribed to free-to-neutral acceptor transition (FA), as shown in panel (*c*) of figure 4. The stable p-type ZnO : (Li,N) annealed at 600 °C shows three dominant peaks located at 3.346 eV, 3.311 eV and 3.219 eV, respectively, as shown in panel (*b*) of figure 4, which is different from the PL spectra of the p-type ZnO : Li [25] and ZnO : N [3, 5]. The excitation power-dependent PL spectrum of the ZnO : (Li,N) annealed at 600 °C was measured at 80 K; it shows that the 3.219 eV band shifts from 3.219 to 3.238 eV with increasing excitation power, as shown in panel (*b*) of figure 5, indicating that the band comes from a recombination of donor-Li–N complex acceptor (DAP).

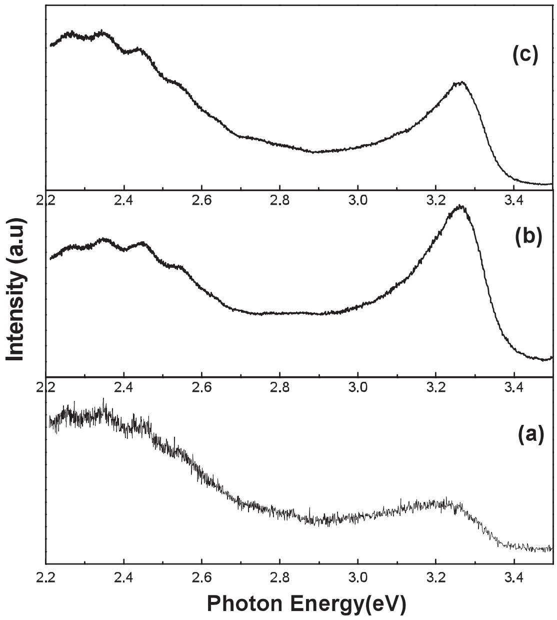

Figure 3. The room-temperature PL spectrum of p-type ZnO : (Li,N) annealed at 500 °C (*a*), 600 °C (*b*) and 700°C (*c*), respectively.

Panel (*a*) of figure 5 shows the temperature-dependent PL measurements. With an increase in the temperature, the position of 3.311 eV peak exhibits red shift, while DAP peak first shows distinctly blue shift and then progressively merges into 3.311 eV band at about 150 K, showing the feature of the thermal ionization of donors [26], which are typical characteristics of FA and DAP transitions [27]. Therefore, it is deduced that the 3.311 eV band comes from emission of free electron to Li–N complex acceptor. The emission line at 3.346 eV is in the range (3.315–3.358 eV) of acceptor bound excitons reported for N [5]-, P [7]- and As [10]- doped p-type ZnO. This specific line has not been reported up to now. It has been ascribed to a $\mathrm{Li_{Zn}}$–N complex, acceptor-bound exciton transition ($\mathrm{A^0X}$).

The optical level of the $\mathrm{Li_{Zn}}$–N complex acceptor can be calculated by the following equation:

$$E_{\mathrm{FA}}(T) = E_{\mathrm{g}}(T) - E_{\mathrm{A}} + \kappa T/2, \qquad (1)$$

where $E_{\mathrm{g}}(T)$ is the temperature-dependent band gap that follow a Varshni-type equation [28] and E_{A}, κ and T are acceptor level, Boltzmann constant and temperature, respectively. Based on the emission peaks of FA at 80 K, the

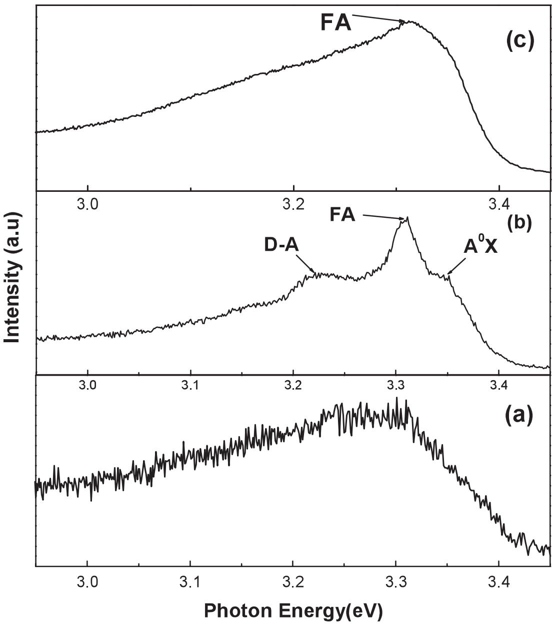

Figure 4. The low-temperature (80 K) PL spectrum of p-type ZnO : (Li,N) annealed at 500 °C (*a*), 600 °C (*b*) and 700 °C (*c*), respectively.

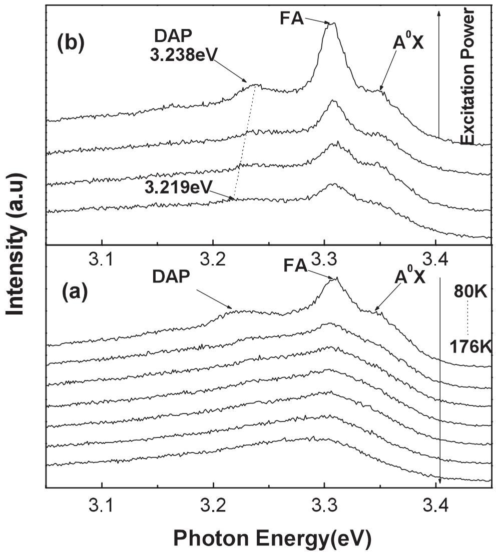

Figure 5. Temperature-dependent PL spectra of p-type ZnO : (Li,N) annealed at 600 °C measured at temperature from 80 up to 176 K (*a*) and excitation power-dependent PL spectra measured at 80 K (*b*).

acceptor level can be calculated by using equation (1) to be about 126 meV.

4. Conclusions

In conclusion, a stable p-type ZnO doped by Li and N was fabricated by RF-magnetron sputtering technique and annealing at 600 °C. It has carrier concentration of 3.07×10^{16} cm^{-3} and Hall mobility of 1.74 cm^2 V^{-1} s^{-1}. The Li occupies Zn site and two N occupy O site, respectively, and the Li bonds with the two N to form Li–N complex acceptors. The p-type conductivity of the ZnO : (Li,N) is mainly due to the Li_{Zn}–N complex acceptor. The acceptor level was estimated to be about 126 meV.

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