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Citation: Appl. Phys. Lett. **97**, 222101 (2010); doi: 10.1063/1.3518059
View online: http://dx.doi.org/10.1063/1.3518059
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v97/i22
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Investigation on the formation mechanism of *p*-type Li–N dual-doped ZnO

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(Received 25 September 2010; accepted 29 October 2010; published online 29 November 2010)

Lithium and nitrogen dual-doped ZnO films [ZnO:(Li, N)] with Li concentrations of 0%–11.2% were grown on sapphire by plasma-assisted molecular beam epitaxy, and a stable *p*-type ZnO:(Li, N) film was obtained by doping 6.1% of Li. The *p*-type conductivity of ZnO:(Li, N) is attributed to the formation of the $\mathrm{Li_i{-}N_O}$ complex, which depresses the compensation of $\mathrm{Li_i}$ donor for $\mathrm{Li_{Zn}}$ acceptor and the generation of $\mathrm{(N_2)_O}$ donors. It is demonstrated that the $\mathrm{Li_i{-}N_O}$ complex can form an impurity band above the valance band maximum, resulting in a decrease in the ionization energy of the acceptor and an improvement in the conductivity and stability of the *p*-type ZnO:(Li, N). © *2010 American Institute of Physics*. [doi:10.1063/1.3518059]

ZnO has attracted much attention for its wide band gap (3.37 eV) and relatively large exciton binding energy (60 meV) at room temperature. It has been regarded as one of the most promising candidates for the next generation of ultraviolet (UV) light emitting diodes and lasing devices. In order to realize the potential application of ZnO, high quality of both *n*- and *p*-type ZnO films is necessary. Now, *n*-type ZnO films can be prepared easily, whereas it is very difficult to obtain stable and reproducible *p*-type ZnO due to high ionization energy of acceptor impurities, low solubility of dopants, and self-compensation effect in ZnO.[1,2] Choosing appropriate acceptor dopant and doping method is proven to be very important in the preparation of *p*-type ZnO. Great efforts have been made to obtain *p*-type ZnO by doping group I and V elements in the recent years.[3,4] Theoretical calculations predicted that lithium (Li) and nitrogen (N) are the best candidates due to the matching of atomic radius with Zn and O and shallow acceptor levels. However, Li prefers to occupy the interstitial sites ($\mathrm{Li_i}$), acting as the donor, rather than the Zn sites ($\mathrm{Li_{Zn}}$), acting as the acceptor. Moreover, it is proven that $\mathrm{Li_i}$ can migrate easily in ZnO,[5] which increases the possibility of compensation between $\mathrm{Li_i}$ and acceptors. To solve such problems, a codoping method of Li and N is used to fabricate *p*-type ZnO films, which is expected to depress the compensation of $\mathrm{Li_i}$ donor for $\mathrm{Li_{Zn}}$ acceptor and the migration of $\mathrm{Li_i}$ by the formation of the $\mathrm{Li_i{-}N_O}$ complex. Although there are several reports on the preparation of stable *p*-type ZnO films by using Li and N as dopants [denoted as ZnO:(Li, N)],[4,6] the chemical state of the acceptor dopants and the formation mechanism of the *p*-type conductivity are still unclear.

In order to identify the acceptor states of ZnO:(Li, N), undoped ZnO (denoted as ZnO) and ZnO:(Li, N) films with different Li doping concentrations were prepared on *c*-sapphire substrates by plasma-assisted molecular beam epitaxy (P-MBE) with highly pure metal Zn and Li as well as NO. The crystal structure of the films was characterized by x-ray diffraction (XRD) with Cu $K\alpha_1$ radiation ($\lambda = 0.154\,18$ nm); x-ray photoelectron spectroscopy (XPS) was used to detect the composition and chemical state of Li and N. The optical band gaps of the thin films are measured by using an UV-vis-near infrared spectrophotometer at room temperature.

The XRD measurement shows that both ZnO and ZnO:(Li, N) films have a wurtzite structure with (002) preferential orientation and lattice constant of the ZnO:(li, N) in *c* axis (denoted as *c*) increases with increasing Li concentration (not shown). It is well known that Li doped in ZnO has two chemical states of $\mathrm{Li_i}$ donor and $\mathrm{Li_{Zn}}$ acceptor and that $\mathrm{Li_i}$ increases the *c* while $\mathrm{Li_{Zn}}$ reduces it. Therefore, the increment of the *c* implies the existence of many $\mathrm{Li_i}$ in the ZnO:(Li, N).

The electrical properties of the ZnO and ZnO:(Li, N) films were measured by the Hall effect measurement system, as listed in Table I. It shows that the ZnO film behaves as *n*-type conductivity. When the Li concentration is 3.6%, the ZnO:(Li, N) films still exhibit an *n*-type conductivity, but the electron concentration decreases, in comparison with ZnO. When the Li concentration increases to 6.1%, the ZnO:(Li, N) film changes from *n*-type conductivity to *p*-type conductivity and has kept the *p*-type conductivity stable. To verify the reliability of the *p*-type ZnO:(Li, N), a *p*-ZnO:(Li, N)/*n*-ZnO homojunction was fabricated on a sapphire substrate. A typical *I*-*V* rectification was observed with a turn on voltage of 4.5 V and a reverse breakdown voltage of 12.5 V,

TABLE I. Electrical properties of ZnO:(Li, N) thin films doped with different Li concentrations.

Li (at. %)	Resistivity (Ω cm)	Mobility ($\mathrm{cm^2/V\,s}$)	Carrier concentration ($\mathrm{cm^3}$)	Carrier type
0	0.05	36.79	3.67×10^{18}	*n*
3.6	1.87	4.25	8.01×10^{17}	*n*
6.1	60	1.36	8.22×10^{16}	*p*
11.2	Insulating	⋯	⋯	⋯

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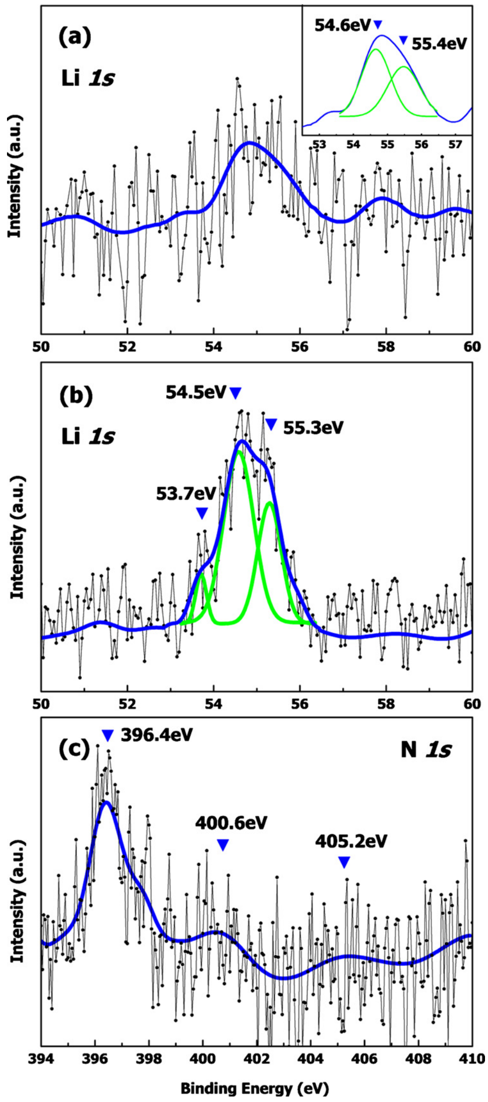

FIG. 1. (Color online) XPS core lines and peak fit of [(a) and (b)] Li_{1s} of the ZnO:($Li_{6.1\%}$, N) and ZnO:($Li_{11.2\%}$, N) films; the inset shows the Gauss fitting of the Li_{1s} peak; (c) N_{1s} of the ZnO:($Li_{6.1\%}$, N) films.

which demonstrates that the conductivity of the *p*-ZnO:(Li, N) is reliable. Further increasing the Li concentration, the ZnO:(Li, N) film becomes an insulator. The insulating properties are usually due to the compensation of the Li_i donor for Li_{Zn} acceptor and other native acceptors [such as Zn vacancies (V_{Zn})]. The change of the electrical properties of the ZnO:(Li, N) is different from that of Li monodoped ZnO (ZnO: Li), which is usually insulating.

In order to understand the formation mechanism of the *p*-type ZnO:(Li, N), the chemical states of Li and N in the ZnO:(Li, N) films were identified by XPS measurements. Figure 1(a) presents the Li_{1s} spectrum of the ZnO:(Li, N) film with 6.1% of Li, which can be fitted by two subspectra located at 54.6 and 55.4 eV, respectively, using the Gaussian fitting method, as shown in the inset. Since the 55.4 eV is close to the binding energy of Li_{1s} of Li–O bond in the Li_2O film,[7] the 55.4 peak can be assigned to Li_{Zn}. Arof *et al.*[8] proved that the binding energy of Li_{1s} bonding with N is in the range of 54.0–54.8 eV in the materials containing Li and N. Thus, the peak located at 54.6 eV can be assigned to Li_{1s} in a Li–N bond, implying that Li bonds with N in the ZnO:(Li, N). Figure 1(b) shows the Li_{1s} spectrum of the ZnO:(Li, N) film with 11.2% of Li, which is fitted by three peaks, located at 53.7, 54.5, and 55.3 eV, respectively. As in the discussion above, the 54.5 and 55.3 eV peaks are associated with Li in the Li–N bond and Li_{Zn}, respectively. The peak located at 53.7 eV can be attributed to Li_i, according to the results of Yi *et al.*[7] Figure 1(c) shows the N_{1s} spectrum of the ZnO:(Li, N) film with 6.1% of Li, which reveals three peaks, located at 396.4, 400.6, and 405.2 eV, respectively. The peak located at 400.6 eV is assigned to the C–N bond.[9] The peaks at 396.4 and 405.2 eV are very close to the binding energy of the N_{1s} of N_O and $(N_2)_O$ in N-doped ZnO, respectively,[10] so the 396.4 and 405.2 eV peaks are attributed to the N_{1s} of N_O and $(N_2)_O$, respectively. Due to the existence of repulsive Coulomb interaction between $Li_{Zn}{}^{+1}$ and $N_O{}^{+1}$, it is impossible to form $Li_{Zn}-N_O$ complex, which is in agreement with the theoretical calculation results.[11] Therefore, the Li_{1s} peak located at 54.6 eV should originate from Li in the Li_i-N_O complex. The formation of the Li_i-N_O complex depresses the compensation of Li_i for Li_{Zn} acceptor. In addition, as Fig. 1(c) shows, the XPS peak of $(N_2)_O$ is very weak, and the N_O peak is dominant in the ZnO:(Li, N) films. Compared with the XPS spectra of the N-doped ZnO produced by using NO and N_2 as N dopants,[12,13] the $(N_2)_O$ peak intensity of ZnO:(Li, N) film is much weaker than that of the N monodoped ZnO film, implying that the formation of the Li_i-N_O complex may depress the $(N_2)_O$ doping. The above discussions indicate that the formation of the Li_i-N_O complex is favorable to the formation of *p*-type ZnO.

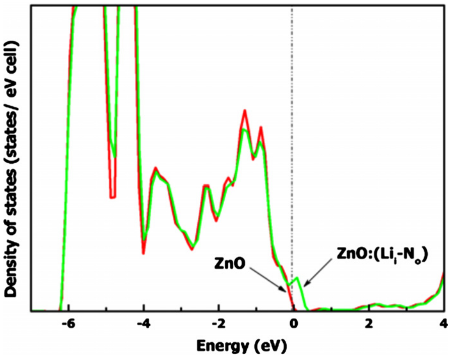

FIG. 2. (Color online) The total density of states of the undoped ZnO and ZnO: (Li, N) systems; the VBM of undoped ZnO and ZnO:(Li, N) is presented with dashed line.

In order to demonstrate the formation of the Li_i-N_O complex, the effect of the Li_i-N_O complex on the electron structure of ZnO:(Li, N) was investigated by first-principles density-functional theory and optical absorption. Obviously, the Li_i-N_O complex is dielectric; it cannot provide electron or hole in ZnO:(Li, N), but may affect the electrical properties by changing the electronic structure, based on semiconductor theory. Therefore, we performed a first-principles calculation in order to understand well the electronic structure of the Li_i-N_O complex in ZnO. A 72 atom wurtzite supercell is used for the defect calculations. Li atom is placed in an octahedral interstitial site and N atom substitutes the nearest neighbor oxygen site. Figure 2 shows the calculated total density of states for the pure ZnO host and a supercell containing a complex of Li_i-N_O, which indicates that the formation of the Li_i-N_O complex does not change the basic electronic structure, but generates an additional fully occupied impurity band above the valance band maximum (VBM), resulting in an upward shift of the VBM and a de-

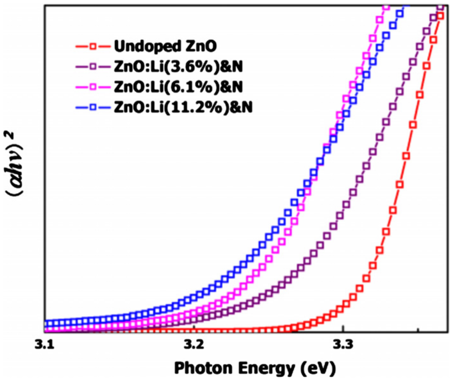

FIG. 3. (Color online) Variation of $(\alpha h\nu)^2$ with photon energy $(h\nu)$ of ZnO thin films as a function of the Li doping concentration.

crease in the band gap. The electron transition will occur between the acceptor defect levels and the impurity bands, rather than the valence band, which makes the ionization energy of acceptor lower. As we expect, the upward shift of the VBM will improve the stability and conductivity of the *p*-type ZnO.

To confirm this calculation result, the band gaps of the ZnO:(Li, N) and ZnO films are investigated by using optical absorption spectra. Figure 3 shows the $(\alpha h\nu)^2$ of the ZnO and ZnO:(Li, N) with various Li concentrations as a function of the photon energy, where the α is absorption coefficient and $h\nu$ is the photon energy. For direct band gap semiconductor, the relationship between α and band gap E_g can be written as[14]

$$\alpha(hv) = B[(hv - E_g)^{1/2}/hv], \tag{1}$$

where the coefficient B is a parameter related to the band tail states. By using the data in Fig. 3 and Eq. (1), the band gap of ZnO and ZnO:(Li, N) with Li contents of 3.6%, 6.1%, and 11.2% were evaluated to be 3.282, 3.224, 3.176, and 3.152 eV, respectively, indicating that the band gap becomes narrow as Li and N are incorporated into ZnO and decreases with increasing Li concentration, in agreement with the calculation results mentioned above.

Based on our calculated and experimental results, it is deduced that $\mathrm{Li_i}$ can combine with $\mathrm{N_O}$ to form the $\mathrm{Li_i{-}N_O}$ complexes in ZnO:(Li, N) and the $\mathrm{Li_i{-}N_O}$ complexes forms impurity band above the VBM. The former can depress the compensation of $\mathrm{Li_i}$ for acceptor, favoring *p*-type doping of the ZnO, and the latter can decrease the ionization energy of the acceptor, being favorable to improving the conductivity and stability of the *p*-type ZnO.

According to the discussion mentioned above, the formation mechanism of the *p*-type ZnO:(Li, N) can be given qualitatively as follows: when Li and N are incorporated into ZnO simultaneously, $\mathrm{Li_i}$ will combine with $\mathrm{N_O}$ to form $\mathrm{Li_i{-}N_O}$ complex, which depresses the compensation of $\mathrm{Li_i}$ for the $\mathrm{Li_{Zn}}$ acceptor. Obviously, the amount of $\mathrm{Li_{Zn}}$ increases with increasing Li doping concentration in some ranges. Therefore, when Li doping concentration is low, the uncompensated $\mathrm{Li_{Zn}}$ is not enough to compensate for the intrinsic donor defect. ZnO:(Li, N) behaves as *n*-type conductivity in low doping concentration with the decrease in electron concentration. When the amount of the uncompensated $\mathrm{Li_{Zn}}$ is larger than that of intrinsic donor defects with further increasing Li concentration, ZnO:(Li, N) changes from *n*-type to *p*-type conduction, as shown in Table I. With further increasing Li concentration, some $\mathrm{Li_i}$ may not combine with $\mathrm{N_O}$ to form $\mathrm{Li_i{-}N_O}$ complex due to the limited solubility of $\mathrm{N_O}$ in ZnO, leading to excessive $\mathrm{Li_i}$. As shown in Fig. 1(b), an additional Li_{1s} peak associated with $\mathrm{Li_i}$ is observed in ZnO:(Li, N) with 11.2% Li, implying that some $\mathrm{Li_i}$ do not combine with $\mathrm{N_O}$ to form $\mathrm{Li_i{-}N_O}$ complexes. The excessive $\mathrm{Li_i}$ will compensate for the $\mathrm{Li_{Zn}}$ acceptor, resulting in that the hole concentration begins to decrease, even that the conductivity of the ZnO:(Li, N) changes from *p*-type to insulating at higher Li doping concentration, as observed in Li monodoped ZnO.

In summary, the ZnO:(Li, N) films were grown on sapphire by P-MBE, their conductivities change from *n*-type to *p*-type and then to insulating with increasing Li concentration, and the stable *p*-type ZnO:(Li, N) was obtained by doping 6.1% of Li. It is demonstrated in theory and experiment that the formation of *p*-type ZnO:(Li, N) is attributed to the formation of the $\mathrm{Li_i{-}N_O}$ complex. On one hand, the $\mathrm{Li_i{-}N_O}$ complex depresses the compensation of the $\mathrm{Li_i}$ donor for $\mathrm{Li_{Zn}}$ acceptor and the generation of $\mathrm{(N_2)_O}$ donors, leading to the existence of uncompensated $\mathrm{Li_{Zn}}$ acceptors. On the other hand, it can form an impurity band above VBM, resulting in a decrease in the ionization energy of the acceptor and an improvement in the conductivity and stability of the *p*-type ZnO.

This work was supported by the Key Project of National Natural Science Foundation of China under Grant No. 50532050, the "973" program under Grant No. 2006CB604906, the National Natural Science Foundation of China under Grant Nos. 6077601, 60506014, 10674133, 60806002, and 10874178, and the Swedish Research Links via VR.

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