Identification of acceptor states in Li-doped *p*-type ZnO thin films

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We investigate photoluminescence from reproducible Li-doped *p*-type ZnO thin films prepared by dc reactive magnetron sputtering. The Li_{Zn} acceptor state, with an energy level located at 150 meV above the valence band maximum, is identified from free-to-neutral-acceptor transitions. Another deeper acceptor state located at 250 meV emerges with the increased Li concentration. A broad emission centered at 2.96 eV is attributed to a donor-acceptor pair recombination involving zinc vacancy. In addition, two chemical bonding states of Li, evident in x-ray photoelectron spectroscopy, are probably associated with the two acceptor states observed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2236225]

Research activity on ZnO has increased over the past few years, with particular interest in potential optoelectronic applications. This is because of its large exciton binding energy of 60 meV and the availability of large-area ZnO substrates. However, the realization of *p*-type ZnO has proven difficult due to the asymmetric doping limitations,[1] and currently is the bottleneck in the development of ZnO-based devices. The optimal choice of acceptor species remains to be determined, with a number of candidates receiving particular attention. N substituting for O appears promising.[2–5] Other group-V dopants with large size mismatches, such as P and As, have also been explored.[6–8] Group-I species substituting for Zn, such as Li_{Zn}, are theoretically predicted to have a shallow acceptor level.[9] However, more detailed theoretical calculations give different sentiments toward the outlook of Li-doped ZnO. On a positive side, Lee and Chang proposed that H can help to increase the solubility of Li and subsequent H removal can potentially result in low-resistivity *p*-type ZnO.[10] On a negative side, Wardle *et al.* suggested that *p*-type doping may be limited by the formation of complexes, such as $Li_{Zn}-Li_i$, $Li_{Zn}-H$, and $Li_{Zn}-AX$.[11] In our previous studies, we have demonstrated the growth of *p*-type ZnO thin films by Li doping.[12,13] In this letter, we use a combination of photoluminescence (PL) and x-ray photoelectron spectroscopy (XPS) to shed more light on the role of Li in *p*-type ZnO.

Li-doped ZnO thin films were grown on glass substrates by dc reactive magnetron sputtering method. The detailed growth procedures were published elsewhere.[12,13] A series of sputtering targets with different Li contents, namely, 0.1, 0.5, 1, and 2 at. %, was employed in this study, and henceforth the ZnO thin films grown using these sputtering targets will be referred to as $ZnO:Li_{0.001}$, $ZnO:Li_{0.005}$, $ZnO:Li_{0.01}$, and $ZnO:Li_{0.02}$, respectively. All samples were deposited at an optimal substrate temperature of 550 °C. Room temperature Hall-effect measurements were carried out in the van der Pauw configuration (Bio-Rad HL5500PC). Temperature-dependent PL measurements were performed on a Fluorolog-3-Tau fluorescence spectrometer. The chemical states of Li in ZnO were analyzed by XPS using an Omicron EAC2000-125 hemispherical analyzer.

The results of Hall-effect measurements are summarized in Table I. Low-resistivity *p*-type conductivity can only be achieved in the $ZnO:Li_{0.001}$ samples. The optimal results include a resistivity of 16.4 Ω cm, a Hall mobility of 2.65 $cm^2/V\,s$, and a hole concentration of 1.44×10^{17} cm^{-3} with very reproducible characteristics. Samples with high Li contents, i.e., $ZnO:Li_{0.005}$, $ZnO:Li_{0.01}$, and $ZnO:Li_{0.02}$ have high resistivity, low carrier concentration, and low Hall mobility. For these high Li-content samples, the electrical properties are insensitive to the magnitude of Li. Note that Hall-effect measurements on the high-resistivity samples can result in ambiguous determination of carrier type, due to their low Hall mobility and low carrier concentration. Similar noise signal for ZnO has also been observed and treated as *p* type.[14] On the other hand, the low-resistivity samples with a hole concentration above 10^{17} cm^{-3} always give a definitive *p*-type signal. In our previous study, the degradation of *p*-type conductivity in our higher Li-content samples has been tentatively ascribed to the formation of Li_i or $Li_{Zn}-Li_i$ complex.[12]

To gain more information on the *p*-type doping mechanism of Li, temperature-dependent PL measurements were performed. Figure 1(a) shows the PL spectrum at 8 K for the low-resistivity $ZnO:Li_{0.001}$ sample. The spectrum consists of three bands centered at 3.35, 3.28, and 2.96 eV, labeled as A,

TABLE I. Electrical properties of Li-doped ZnO thin films grown with different Li contents.

Sample	Resistivity (Ω cm)	Hall mobility ($cm^2/V\,s$)	Carrier concentration (cm^{-3})	Carrier type
$ZnO:Li_{0.001}$	16.4	2.65	1.44×10^{17}	*p*
$ZnO:Li_{0.005}$	2.23×10^3	1.08	1.68×10^{15}	*p*
$ZnO:Li_{0.01}$	3.95×10^3	0.83	1.23×10^{15}	*p*
$ZnO:Li_{0.02}$	7.05×10^3	0.66	1.34×10^{15}	*p*

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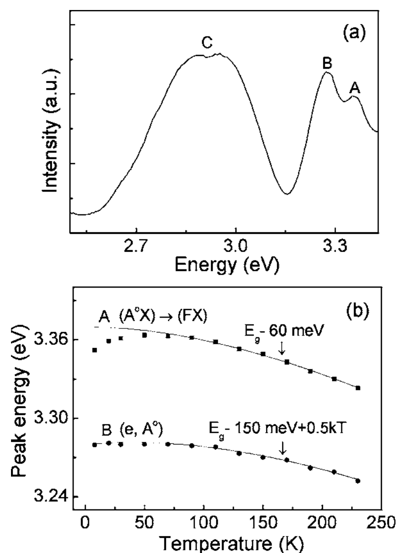

FIG. 1. (a) PL spectrum at 8 K for the ZnO:$Li_{0.001}$ thin film. (b) Temperature-dependent peak positions and their fitting curves for peaks *A* and *B* in (a).

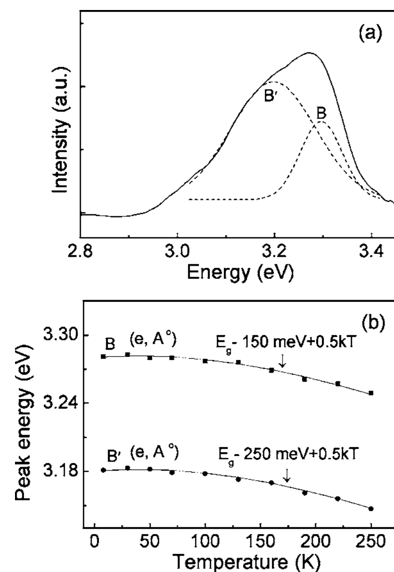

FIG. 2. (a) PL spectrum at 8 K for the ZnO:$Li_{0.01}$ thin film. The dashed lines show the Gaussian fitting curves. (b) Temperature-dependent peak positions and their fitting curves for peaks *B* and *B′* in (a).

B, and C, respectively. We tentatively assign band A to a neutral acceptor-bound exciton emission $(A^\circ X)$ and band B to a free-to-neutral-acceptor (e,A°) transition.

To support our assignment, we analyze the temperature-dependent peak positions of the two bands [Fig. 1(b)]. For band A, an obvious temperature-dependent blueshift from 3.35 eV at 8 K to 3.36 eV at 70 K is observed. We believed that this blueshift is a result of a transition from bound exciton emission to free exciton (FX) emission as temperature increases. A similar transition has also been observed in GaN.[15] In higher temperature range (70–230 K), peak *A* shows a clear FX characteristic with the typical exciton binding energy of 60 meV. As can be seen in Fig. 1(b), the energy of peak *A* fits well with a curve of $E_g(T)-60$ meV. The temperature-dependent band gap is described according to Ref. 16 as

$$E_g(T) = E_g(0) - \alpha T^2/(T+\beta), \quad (1)$$

where α and β are constants and T is temperature. Note that we cannot totally exclude a possibility that the 3.35 eV emission might be a neutral donor-bound exciton emission $(D^\circ X)$. However, considering the low background electron concentration of mid-10^{16} cm^{-3} (Ref. 12) and the definitive *p*-type signals for this sample, it is more likely that this peak comes from $(A^\circ X)$ emission.

The temperature dependence of a peak *B* position fits well in an equation for an (e,A°) transition given by

$$E_{eA}(T) = E_g - E_A + k_B T/2, \quad (2)$$

where $E_{eA}(T)$ is the temperature-dependent (e,A°) transition energy, E_A is the acceptor energy level, and k_B is the Boltzmann constant. The acceptor energy level is found to be 150 meV, which is slightly larger than the electrical (Hall) value from our prior work of 110 ± 10 meV.[12] The higher optical acceptor level (in comparison to the Hall value) is attributed to screening effects (Ref. 17) and can be seen in other semiconductors as well [e.g., GaN (Refs. 18 and 19)]. A perfect match between the experimental values and the fitting curve supports our assignment of the (e,A°) transition. Note that the (e,A°) transition is absent in the nominally undoped ZnO sample grown under the same condition without Li doping. It is, therefore, reasonable to assume that this transition is associated with the Li_{Zn} acceptor.

The broad emission centered at 2.96 eV is believed to be a donor-acceptor pair (DAP) recombination due to its typical blueshifts with the excitation energy (data not shown). The acceptor involved in this DAP recombination is likely to be Zn vacancy due to its low formation energy.[1,20,21] Several works also assigned emission energy in this range (e.g., 3.028 eV at 20 K[22] and 3.09 eV at 6 K[23]) to Zn vacancy. Based on these available literatures, we attribute our broad 2.96 eV emission to a DAP recombination involving zinc vacancy.

For a high-resistivity ZnO:$Li_{0.01}$ sample, the PL spectrum at 8 K can be deconvoluted into two peaks [Fig. 2(a)], centered at 3.28 and 3.18 eV, labeled as B and B′, respectively. As shown in Fig. 2(b), both peaks have temperature dependencies fitting well in the (e,A°) transitions [Eq. (2)], with the acceptor energy levels of 150 and 250 meV.

The exciton emission and the DAP recombination (that is observed in the low-resistivity ZnO:$Li_{0.001}$) disappear in the high-resistivity ZnO:$Li_{0.01}$ sample. The absence of the exciton emission is probably due to the degradation of crystal quality in this high Li-content sample. This is consistent with the observation of the low Hall mobility (Table I). The absence of the DAP recombination can be explained by the suppression of Zn vacancy in ZnO:$Li_{0.01}$. In high Li-content samples, Zn vacancies are more likely to be occupied by Li, forming Li_{Zn} or Li_{Zn}–Li_i complex.

Based on the Hall-effect and PL measurements, it is demonstrated that Li_{Zn} has a shallow acceptor level as theoretically predicted,[9] independent of the Li concentration. The high hole concentration of 1.44×10^{17} cm^{-3}, combined with an (e,A°) transition located at 150 meV [illustrated both in Figs. 1(b) and 2(b)], confirms its shallow nature. Samples with high Li content, e.g., ZnO:$Li_{0.01}$, show another deeper acceptor level at 250 meV. The deeper acceptor level is probably associated with complexes containing Li, such as Li_{Zn}–Li_i and Li_{Zn}–AX.[11] This deeper 250 meV (e,A°) transition becomes dominant in the ZnO:$Li_{0.01}$ sample, which is

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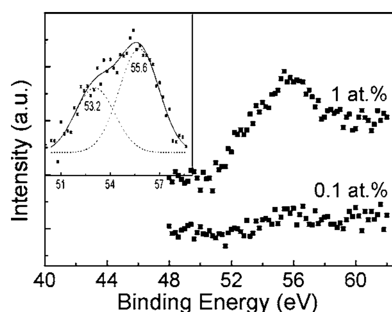

FIG. 3. XPS narrow scan spectra of Li 1*s* for the $ZnO:Li_{0.001}$ and the $ZnO:Li_{0.01}$ samples. The inset shows the Gaussian fitting curves for the $ZnO:Li_{0.01}$ thin film.

consistent with the lower hole concentration observed.

In addition to PL, the chemical bonding states of Li in ZnO were examined by XPS. Figure 3 illustrates the Li 1*s* narrow scan spectra for the $ZnO:Li_{0.001}$ and the $ZnO:Li_{0.01}$ samples. The former spectrum is near the noise level due to the detection limit of XPS. For the $ZnO:Li_{0.01}$ thin film, a peak attributed to Li 1*s* is observed. Gaussian fitting to the spectrum reveals two peaks centered at 53.2 and 55.6 eV, as seen from the inset in Fig. 3. These two chemical bonding states are probably associated with the two acceptor states, in agreement with our PL results in Fig. 2. Further study on their assignment is in progress.

In summary, we have demonstrated reproducible growth of Li-doped *p*-type ZnO thin films by dc reactive magnetron sputtering. A shallow acceptor level of 150 meV is identified from free-to-neutral-acceptor transitions and assigned to the Li_{Zn} acceptor. Another deeper acceptor level of 250 meV, which we tentatively assign to the Li-related complexes, emerges with the increase of Li concentration. We hope that this study, together with other investigations on group-V dopants, will shed light on researches on determination of the optimal choice of acceptor species for ZnO.

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