Dopant source choice for formation of *p*-type ZnO: Li acceptor

Y. J. Zeng, Z. Z. Ye,[a] W. Z. Xu, D. Y. Li, J. G. Lu, L. P. Zhu, and B. H. Zhao
State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

(Received 4 August 2005; accepted 6 January 2006; published online 10 February 2006)

Li-doped, *p*-type ZnO thin films have been realized via dc reactive magnetron sputtering. An optimized result with a resistivity of 16.4 Ω cm, Hall mobility of 2.65 $cm^2/V\,s$, and hole concentration of 1.44×10^{17} cm^{-3} was achieved, and electrically stable over a month. Hall-effect measurements supported by secondary ion mass spectroscopy indicated that the substrate temperature played a key role in optimizing the *p*-type conduction of Li-doped ZnO thin films. Furthermore, ZnO-based *p*-*n* homojunction was fabricated by deposition of a Li-doped *p*-type ZnO layer on an Al-doped *n*-type ZnO layer. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2172743]

ZnO has now gained much attention as a promising material for short-wavelength optoelectronic devices, such as light emitting diodes and laser diodes, because of its large exciton binding energy (60 meV), wide band gap of 3.37 eV at room temperature,[1] and the availability of large-area ZnO substrates. However, the realization of *p*-type ZnO, which is indispensable to practical applications of ZnO-based devices, has thus far proven difficult due to its asymmetric doping limitations.[2] The optimal choice of acceptor species remains to be determined, with a number of candidates receiving particular attention. N substituting for O appears promising;[3–6] While other group-V dopants, such as P and As, have also been investigated.[7,8] Group-I species substituting for Zn, such as Li_{Zn}, theoretically possess shallower acceptor levels.[9] However, contradictory theoretical calculation results have been reported for Li-based *p*-type doping in ZnO. Lee *et al.* proposed a Li–H codoping method for fabricating low-resistivity *p*-type ZnO.[10] Whereas 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] As far as we know, Li doping typically increases the resistivity of otherwise *n*-type ZnO.[12] There have been a few reports on *p*-type ZnO doping with Li. In this letter, *p*-type ZnO thin films were realized via monodoping of Li acceptor by adopting dc reactive magnetron sputtering.

Li-doped ZnO thin films were prepared on glass substrates by dc reactive magnetron sputtering in the O_2-Ar ambient. The insulating glass substrates assured that any *p*-type conduction must come from ZnO thin films without interference from the substrates. The sputtering target was a disk of Zn metal (99.99% purity) mixed with 0.1 at. % Li (99.999% purity). The vacuum chamber was evacuated to a base pressure of 10^{-3} Pa, and then sputtering gases, high purity O_2 (99.999%) and Ar (99.999%), were introduced with a constant total pressure of 4 Pa. The Li-doped ZnO thin films were deposited at the substrate temperature ranging from 450 °C to 600 °C. It should be noted that the background electron concentration for nominally undoped ZnO thin films prepared under the same condition was mid-10^{16} cm^{-3}, which was much lower than 10^{18} cm^{-3} typically reported for sputtering. The O_2/Ar gas ratios as well as the sputtering pressure were optimized to suppress the background carrier concentration. Room temperature and temperature-dependent Hall-effect measurements were carried out in the van der Pauw configuration (BIO-RAD HL5500PC). The depth profile of ZnO thin films was investigated by a CAMECA IMS-3f secondary ion mass spectroscopy (SIMS). Moreover, ZnO-based *p*-*n* homojunction was fabricated by deposition of a Li-doped *p*-type ZnO layer on an Al-doped *n*-type ZnO layer. Ohmic contact between the In–Zn alloy electrode and ZnO thin film was confirmed prior to current-voltage (*I*-*V*) characteristics measurements of the *p*-*n* junction.

The thickness of Li-doped ZnO thin films deposited for 30 min is approximately 350 nm measured by cross-sectional scanning electron microscopy measurement (FEI Sirion 200 FEG SEM). Only two peaks corresponding to (002) and (004) plane of ZnO are observed in the x-ray diffraction pattern [Bede D1 x-ray diffraction system using Cu $K\alpha$ ($\lambda=1.541$ Å), dates not shown], suggesting a high (002) preferential orientation for the Li-doped ZnO thin films. The results of room temperature Hall-effect measurements are summarized in Table I. It is seen that *p*-type conduction can be achieved in all growth temperature ranging from 450 °C to 600 °C. The optimized result is realized at the substrate temperature of 550 °C with a resistivity of 16.4 Ω cm, Hall mobility of 2.65 $cm^2/V\,s$, and hole concentration of 1.44×10^{17} cm^{-3}. The acceptor activation energy is estimated to be 110±10 meV, derived by using the relation $p\propto T^{3/2}\ \exp[-E_A/(k_BT)]$, and the dates of temperature-dependent Hall-effect measurements on the sample grown at 550 °C, as depicted in Fig. 1.

TABLE I. Electrical properties of Li-doped ZnO thin films deposited at different substrate temperatures.

Substrate temperature (°C)	Resistivity (Ω cm)	Hall mobility ($cm^2/V\,s$)	Carrier concentration (cm^{-3})	Carrier type
450	999	0.71	8.67×10^{15}	*p*
500	91.2	2.19	3.13×10^{16}	*p*
550	16.4	2.65	1.44×10^{17}	*p*
600	268.6	2.34	9.98×10^{15}	*p*

[a]Author to whom correspondence should be addressed; electronic mail: yezz@zju.edu.cn

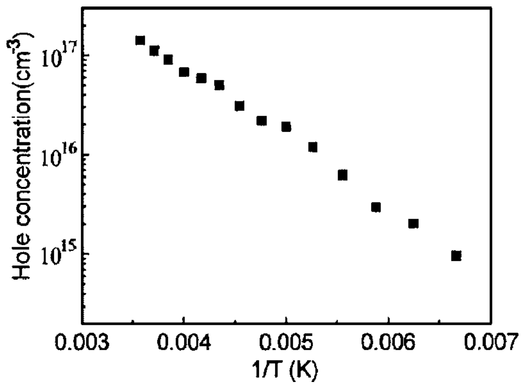

FIG. 1. Temperature-dependent Hall-effect measurements show the variation of hole concentration as a function of inverse temperature for the sample grown at 550 °C.

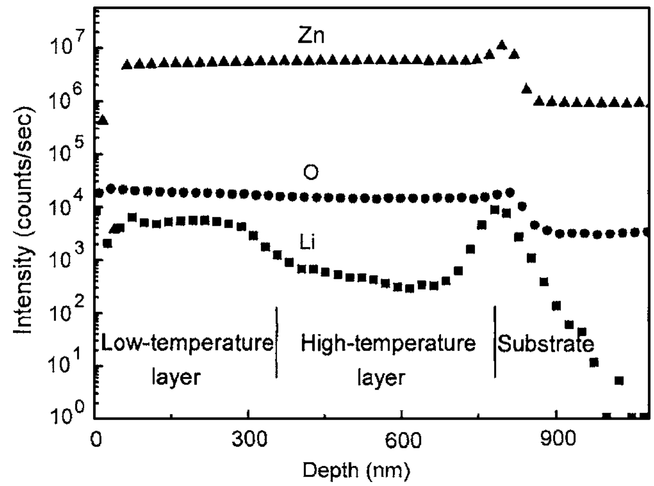

FIG. 3. SIMS depth profiles of Li-doped ZnO thin film grown via a two-step process: 600 °C high-temperature growth followed by 450 °C low-temperature growth.

To investigate the stability of the *p*-type conduction, the sample with the optimized result was re-examined several weeks later. As shown in Fig. 2, the Li-doped ZnO thin film kept *p*-type conduction without any obvious degradation in electrical properties for a month, which confirmed the stability and reproducibility of the *p*-type behavior, identified by Hall-effect measurements.

Further study of the dependence of *p*-type conduction of Li-doped ZnO on substrate temperature was carried out by SIMS measurement. Double-layer-structured Li-doped ZnO thin film was grown via a two-step process: 600 °C high-temperature growth followed by 450 °C low-temperature growth. It is shown in Fig. 3 that the two-layer-structure has been clearly identified, with a thickness of about 350 nm for each layer and the outdiffusion effect for Li element is more evident compared to that of Zn and O. Moreover, it is found that the Li concentration in ZnO decreases with the elevated substrate temperature, which is due to the high vapor pressure of Li species.

Based on the previous Hall effect and SIMS measurements, the mechanism of *p*-type doping in ZnO:Li is proposed tentatively. The Li concentration in ZnO is sensitive to the substrate temperature, as identified by SIMS measurement. Thus, high-temperature growth (600 °C) results in *p*-type ZnO with a low Li acceptor concentration, which is responsible for the relatively low hole concentration of 9.98×10^{15} cm^{-3}. When the substrate temperature decreases to 550 °C, more Li atoms substitute for Zn, which act as an effective acceptor and thus the optimized *p*-type conduction is achieved. With further decrease in substrate temperature, especially to 450 °C, redundant Li atoms are incorporated into the ZnO matrix. It has been theoretically predicted that *p*-type doping in ZnO increases the Madelung energy,[13] which could induce the localization of the acceptor states.[14] Therefore, in the case of low-temperature growth, part of the Li_{Zn} acceptor may be unstable due to the relatively high Madelung energy. The formation of Li_i (Ref. 9) or $Li_{Zn}-Li_i$ complexes[11] is energetically favored, which becomes the limitation for Li-based *p*-type doping in ZnO. This inference can also be supported by Hall-effect measurements, since the sample grown at low temperature of 450 °C possesses low hole concentration of 8.67×10^{15} cm^{-3} and low Hall mobility of 0.71 cm^2/V s. It is the possible Li_i or $Li_{Zn}-Li_i$ defects acting as "hole killer" and scattering center that reduce the hole concentration and Hall mobility evidently. That may also be the reason for the typical high resistivity in Li-doped ZnO.[3,12] However, further investigation on the mechanism of *p*-type doping in ZnO:Li is still in progress.

To further confirm the *p*-type conduction in Li-doped ZnO thin films, ZnO-based *p-n* homojunction was fabricated by deposition of a Li-doped *p*-type ZnO layer on an Al-doped *n*-type ZnO layer, as illustrated in the inset in Fig. 4. In–Zn alloy was used as both *n*-side and *p*-side electrodes, showing linear *I-V* characteristics indicative of good ohmic behavior (Fig. 5). Figure 4 shows the *I-V* characteristics of the ZnO homojunction. The device exhibits rectification for

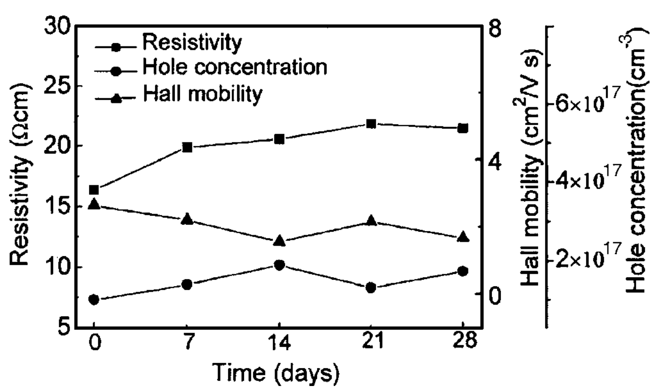

FIG. 2. The results of electrical properties for Li-doped, *p*-type ZnO thin film re-examined several weeks later.

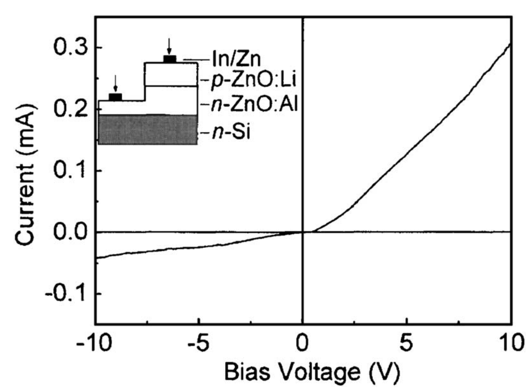

FIG. 4. *I-V* characteristics of ZnO:Li/ZnO:Al *p-n* homojunction measured at room temperature. The inset shows the schematic of the homojunction.

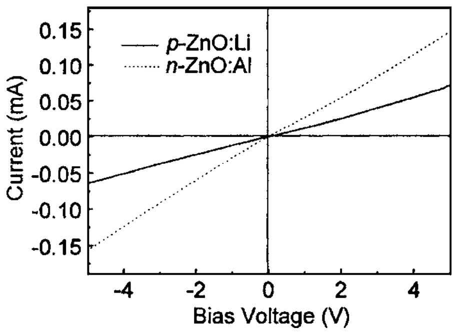

FIG. 5. *I-V* characteristics of In/Zn alloy contacts on *p*-type ZnO:Li and *n*-type ZnO:Al thin films.

repeated measurements, with very reproducible characteristics, which is consistent with the formation of a *p*-*n* junction at the interface.

In conclusion, we have demonstrated the growth of low-resistivity, *p*-type ZnO thin films via monodoping of Li acceptor by adopting dc reactive magnetron sputtering. The acceptable *p*-type conduction, identified by room temperature and temperature-dependent Hall-effect measurements, has been electrically stable over a month. Moreover, ZnO-based *p*-*n* homojunction was fabricated by deposition of a Li-doped *p*-type ZnO thin film on an Al-doped *n*-type ZnO film, which provides another dopant source choice for formation of *p*-type ZnO.

This work was supported by National Natural Science Foundation of China under Contract No. 50532060, National Natural Science Foundation of China under Contract No. 50572095, and Zhejiang Provincial Natural Science Foundation of China under Grant No. Y405126.

[1] Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
[2] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[3] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[4] J. F. Rommeluere, L. Svob, F. Jomard, J. Mimila-Arroyo, A. Lusson, V. Sallet, and Y. Marfaing, Appl. Phys. Lett. **83**, 287 (2003).
[5] W. Z. Xu, Z. Z. Ye, T. Zhou, B. H. Zhao, L. P. Zhu, and J. Y. Huang, J. Cryst. Growth **265**, 133 (2004).
[6] J. G. Lu, Z. Z. Ye, F. Zhuge, Y. J. Zeng, B. H. Zhao, and L. P. Zhu, Appl. Phys. Lett. **85**, 3134 (2004).
[7] K. K. Kim, H. S. Kim, D. K. Hwang, J. H. Lim, and S. J. Park, Appl. Phys. Lett. **83**, 63 (2003).
[8] D. C. Look, G. M. Renlund, R. H. Burgener, and J. R. Sizelove, Appl. Phys. Lett. **85**, 5269 (2004).
[9] C. H. Park, S. B. Zhang, and S.-H. Wei, Phys. Rev. B **66**, 073202 (2002).
[10] E. C. Lee and K. J. Chang, Phys. Rev. B **70**, 115210 (2004).
[11] M. G. Wardle, J. P. Goss, and P. R. Briddon, Phys. Rev. B **71**, 155205 (2005).
[12] N. R. Aghamalyan, E. Kh. Goulanian, R. K. Hovsepyan, E. S. Vardanyan, and A. F. Zerrouk, Phys. Status Solidi A **199**, 425 (2003).
[13] T. Yamamoto and H. Katayama-Yoshida, J. Cryst. Growth **214/215**, 552 (2000).
[14] T. Yamamoto, Jpn. J. Appl. Phys., Part 1 **42**, 514 (2003).