Fabrication of *p-n* junctions in as-grown ZnMgO/ZnO films

Hyuck Soo Yang, Y. Li, D. P. Norton, and S. J. Pearton
Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611

Soohwan Jang and F. Ren
Department of Chemical Engineering, University of Florida, Gainesville, FL 32611

L. A. Boatner
Oak Ridge National Laboratory, Oak Ridge, TN 37831

ABSTRACT

We achieved *p*-(Zn,Mg)O by doping with phosphorous and the conduction type was confirmed by capacitance-voltage properties of metal/insulator/*p*-(Zn,Mg)O:P diode structures as well as Hall measurements. The *p*-(Zn,Mg)O:P/*n*-ZnO junction was grown by pulsed laser deposition on bulk ZnO doped with Sn. Without post-growth annealing, the phosphorous-doped ZnMgO showed *p*-type conductivity (hole density ~10^{16} cm^{-3}, mobility ~6 $cm^2 \cdot V^{-1} \cdot s^{-1}$) in the as-grown state. The metal contacts in top-to-bottom *p-n* junctions were made with Ni/Au as the *p*-ohmic and Ti/Au as the backside *n*-ohmic contact. The *p*-contacts showed improved characteristics after annealing up to 350 - 400 °C, but the *n*-contacts were ohmic as-deposited. The simple, low temperature growth (≤500 °C) and processing sequence (≤400 °C) shows the promise of ZnO for applications such as low-cost UV light emitters and transparent electronics.

I. INTRODUCTION

ZnO has been actively investigated for its potential applications in transparent electronics, gas sensors, spin functional devices and UV light emitters.[1-11] In the case of UV light emitters, ZnO has some particular advantages including higher exciton binding energy (~60 meV) compared to GaN (~25 meV) and the ready availability of relatively large, high quality substrates, enabling the fabrication of vertical geometry devices with low threading dislocation densities. While the lateral type GaN-based light-emitting diodes (LEDs) have limitations such as current crowding and ineffective light extraction, vertical type LEDs demonstrates improved light output and power conversion efficiency along with the increased light emitting area and facilitation of device fabrication.[12] ZnO can also be grown at lower epitaxial growth temperatures and is readily patterned in simple wet etchants. There have been many recent reports of achieving *p*-type doping using pulsed laser deposition (PLD), sputtering, evaporation and molecular beam epitaxy.[13-21] All of this progress has focused attention on development of LEDs in the ZnMgO/ZnO heterostructure system. Alivov *et al.*[22-23]

Fifth International Conference on Solid State Lighting, edited by Ian T. Ferguson, John C. Carrano, Tsunemasa Taguchi, Ian E. Ashdown, Proc. of SPIE Vol. 5941
(SPIE, Bellingham, WA, 2005) · 0277-786X/05/$15 · doi: 10.1117/12.616668

and Osinsky *et al.*[24] have recently reported electroluminescence (EL) from *p*-(Al)GaN/*n*-ZnO junctions, while Tsukazaki *et al.* [2] obtained violet EL from ZnO homojunctions grown on $ScAlMgO_4$ substrates. We achieved *p*-(Zn,Mg)O by doping with phosphorous and the electrical type was confirmed by capacitance-voltage properties of metal/insulator/*p*-(Zn,Mg)O:P diode structures as well as Hall measurements.[25] For the realization of successful ZnO-based optoelectronic devices, it is essential to make high-quality ohmic contacts with low specific contact resistance. Various metallization schemes for ohmic contacts to *n*-ZnO, mostly films, have been reported, for example, Ti/Au[26], Al/Au[27], Ti/Al[28], Ru[29], Ta/Au[30], Al/Pt[31], Al[32], Ti/Al/Pt/Au[33] and Re/Ti/Au.[34] They showed specific contact resistance values in the range of $10^{-2}\sim10^{-7}$ Ωcm^2, depending upon the annealing temperature and the carrier concentration of the *n*-ZnO. In the case of *p*-type ohmic contacts, several groups have demonstrated that Au, Ni and Pt contacts can be used as ohmic metallization on thin films of *p*-type ZnO or ZnMgO deposited on sapphire or ITO-coated glass substrates.[35-37]

In this paper, we report on the characteristics of as-grown $(Zn_{0.9}Mg_{0.1})O$/ZnO *p-n* junctions grown by PLD on bulk, Sn-doped, n^+-ZnO substrates. The heavily doped ZnO substrate allows achievement of good ohmic contacts with unannealed Ti/Au, reducing the series resistance in the device.

II. EXPERIMENTAL

The substrates were Sn-doped, bulk ZnO grown by vapor transport at Oak Ridge National Laboratories. The electron concentration at room temperature was $\sim10^{19}$ cm^{-3}, with mobility of 60 $cm^2\cdot V^{-1}\cdot s^{-1}$. Phosphorus-doped $(Zn_{0.9}Mg_{0.1})O$ targets were fabricated using high-purity ZnO (99.9995%) and MgO (99.998%) powders, with P_2O_5 (99.998%) serving as the doping agent. Use of the (Zn,Mg)O alloy reduces the residual *n*-type conductivity which is caused by shallow defect donor states. The ablation targets were fabricated with a phosphorus doping level of 2 at.%.

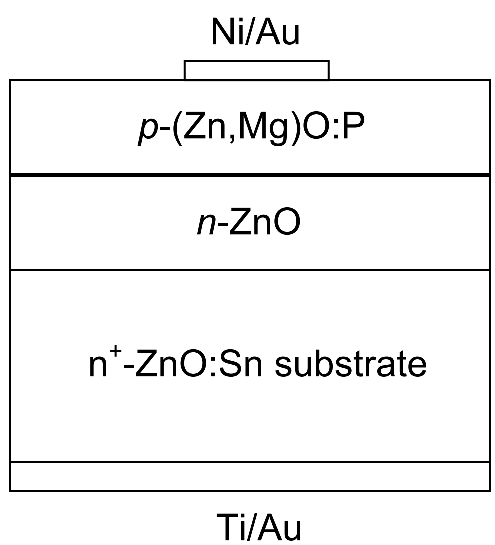


Figure 1. Schematic of (Zn,Mg)O/ZnO p-n junction structure.

The KrF excimer laser (λ=248 nm) with repetition rate of 1 Hz and pulse energy density of 1-3 J/cm^2 was used as the ablation source. The ZnO growth chamber exhibits a base pressure of ~1×10^{-6} Torr. Film growth of the layer structure shown in Fig. 1 was performed at 500 ˚C for ZnMgO and 400 °C for ZnO in an oxygen pressure of 50-150 mTorr. An *n*-type ZnO layer 0.5 μm thick with electron concentration of 10^{17} cm^{-3} and mobility of 25 cm$^2\cdot$V$^{-1}\cdot$s^{-1} was grown first, followed by a 0.6 μm thick ZnMgO layer with hole concentration of ~ 10^{16} cm^{-3} and mobility of 6 cm$^2\cdot$V$^{-1}\cdot$s^{-1}, determined from van der Pauw Hall measurements carried out on separate single-layer calibration samples. The *p*-side of the structures were contacted with Ni/Au (100 Å/400 Å) deposited by e-beam evaporation and patterned by lift-off with contact diameters ranging from 50 μm to 375 μm. We measured the current-voltage (I-V) characteristics of these contacts between pads in a transmission line pattern for annealing temperatures up to 450 °C. After the p-contact deposition and annealing, the bulk ZnO substrate was given a Ti/Au (200 Å/1000 Å) full-backside contact that was not annealed. The I-V characteristics of the resulting *p-n* junction diodes were measured using an Agilent 4156C parameter analyzer. The measurement temperature was controlled with a Wentworth Labs Tempchuck TC-100, ranging from 25 to 200 °C.

III. RESULTS AND DISCUSSION

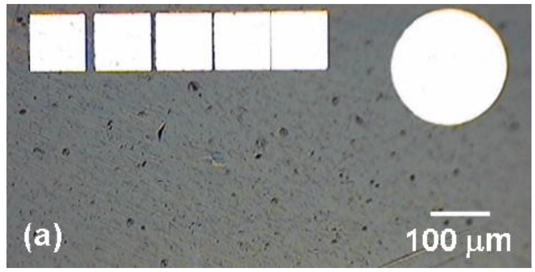
I-V characteristics at 25 °C from the *p*-side metallization were obtained between two square contact pads 100 μm on a side as a function of the annealing temperature, as shown in Fig. 2. The as-deposited contacts showed weak rectifying behavior but the linearity of the contacts improved with annealing temperature up to ~400 °C and showed typical characteristics of *p*-contacts formed on *p*-GaN:Mg with relatively low hole densities due to the high ionization energy of the acceptor dopant (Mg in that case). The specific contact resistance was 1×10^{-2} $\Omega\cdot$cm^2. For a low carrier density system such as *p*-ZnMgO in which the thermionic model is operative, the measurement temperature dependence of the specific contact resistance, r_c, is given by

$$r_c = (k/eA^*T)\exp(e\Phi_B/kT)$$

where k is Boltzman's constant, e the electronic charge, A^* Richardson's constant, T the absolute temperature and Φ_B the barrier height.

Figure 3 shows a semilogarithmic plot of specific contact resistance as a function of measurement temperature. The effective barrier height is found to be 0.39±0.01 eV, when we use a calculated value of 32 Acm^{-2}K^{-2} for the Richardson's constant with the assumption that the effective hole mass is $0.27m_o$. Note that the specific contact resistance is reduced significantly at higher temperatures, reaching a value of 4×10^{-5} Ωcm^2 at 473 K. This occurs at least partially because of the increased ionization efficiency of the P acceptors in the ZnMgO, which from a simple calculation is expected to lead to an increase in hole density approximately by a factor of 3 between 293-473 K.

Indeed, the ZnMgO sheet resistance was found to decrease by almost an order of magnitude over this temperature range along with the decrease in contact resistance. This shows that the contacts will be effective for high temperature UV light-emitting devices.



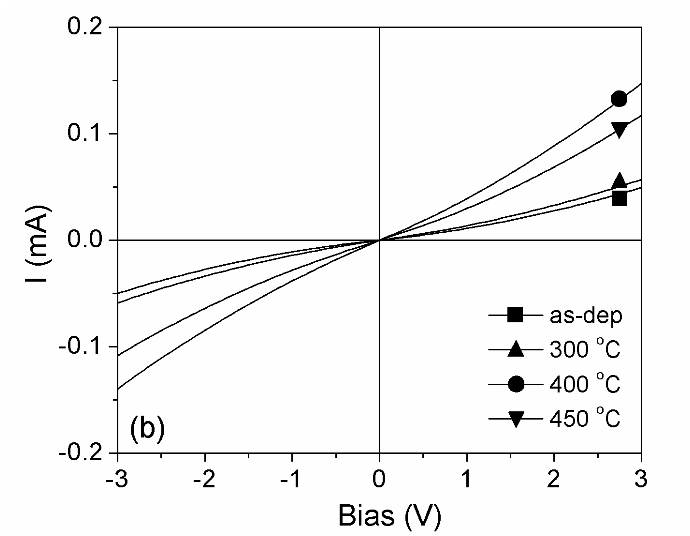


Figure 2. (a) Optical micrograph and (b) I-V characteristics measured at 25 °C of Ni/Au contacts on *p*-(Zn,Mg)O. The I-V characteristics between two contact pads were measured as a function of the annealing temperature used.

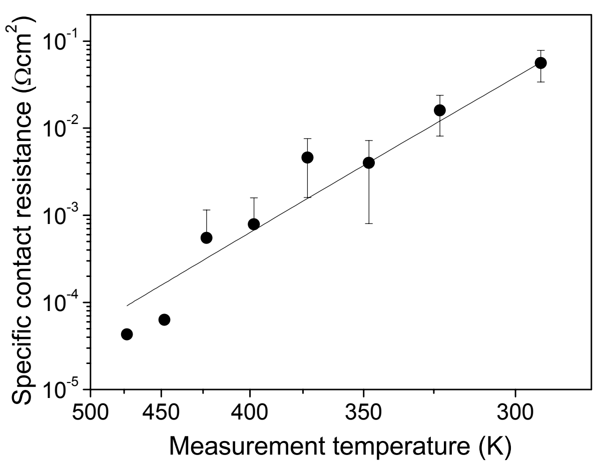


Figure 3. Semilogarithmic plot of the specific contact resistance of Ni/Au contacts to p-(Zn,Mg)O as a function of measurement temperature.

E-beam deposited Ti/Au contacts were ohmic in the as-deposited state, facilitated by the high *n*-type doping of the substrate. It is reported that very thin titanium oxide

layer can be formed at the interface when the Ti is contacted to ZnO even in as-deposited condition[38] since the titanium has a higher affinity with oxygen than Zn (ΔH_f^o (Ti_3O_5)= -2459.1 kJ/mol, ΔH_f^o (Ti_2O_3)= -1520.9 kJ/mol, ΔH_f^o (TiO_2)= -944 kJ/mol, ΔH_f^o (TiO)= -542.7 kJ/mol *vs.* ΔH_f^o (ZnO)= -350kJ/mol)[39]. As a result, the oxygen vacancies, which are effective electron donors, increase carrier concentration near the ZnO surface promoting the tunneling phenomena through the extremely thin oxide barrier.

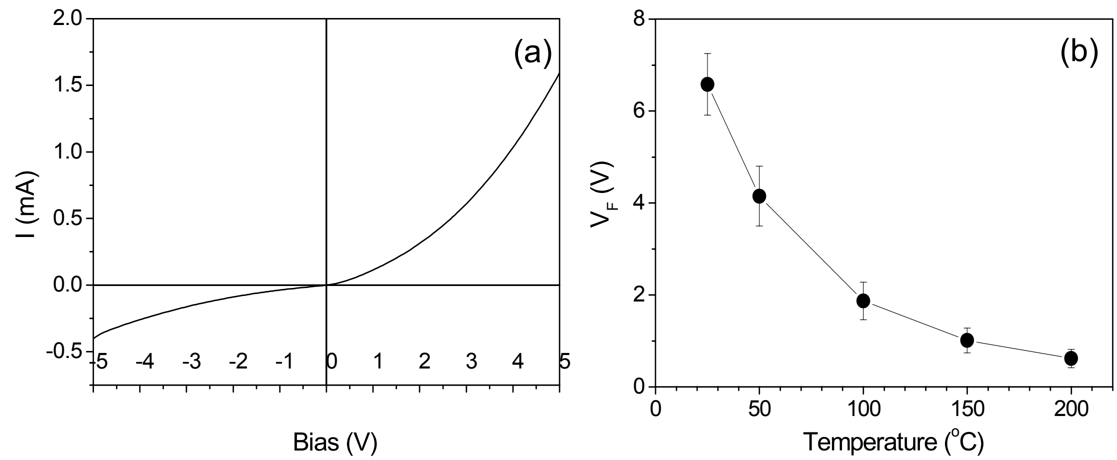


Figure 4. (a) I-V characteristics of ZnMgO/ZnO *p-n* junctions measured at 25 °C, and (b) Measurement of temperature dependence of the forward turn-on voltage.

Figure 4(a) shows the I-V characteristics from the top-to-bottom structure, exhibiting rectifying behavior. Since rectifying behavior also can arise from the metal Schottky contact, we verified the ohmic behavior between adjoining Ni/Au contacts on top of the ZnMgO:P. (i.e., measurement in a lateral direction produced ohmic behavior while the vertical structure showed rectifying characteristics, confirming the presence of a *p-n* junction.) The devices showed rectification up to measurement temperatures of ~200 °C, with very reproducible characteristics. Figure 4(b) shows the measurement of temperature dependence of the forward turn-on voltage (V_F), defined as the voltage at a current density of 10 A·cm^{-2}. The turn-on voltage decreases with increasing temperature, as would be expected from the increasing ionization efficiency of the P acceptors in the ZnMgO producing a higher hole concentration in that layer.

IV. CONCLUSIONS

In conclusion, we have demonstrated growth at ≤500 °C of *p*-ZnMgO/*n*-ZnO junctions on Sn-doped ZnO substrates. No post-growth annealing was needed to achieve *p*-type conductivity in the P-doped ZnMgO. The diode fabrication process used a maximum temperature of 400 °C, showing the potential of ZnO for simple, low-cost lighting and display applications.

ACKNOWLEDGMENTS

This research was sponsored by the Army Research Office under grant no. DAAD19-01-1-0603, the Army Research Laboratory, the National Science Foundation (DMR 0400416, Dr. L. Hess), and the Air Force Office of Scientific Research (Dr. Todd Steiner) under grant F49620-03-1-0370.

REFERENCES

[1] S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, Prog. Mater. Sci. **50**, 293 (2005).
[2] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nat. Mater. **4**, 42 (2005).
[3] S. J. Pearton, Y. W. Heo, M. Ivill, D. P. Norton, and T. Steiner, Semicond. Sci. Technol. **19**, R59 (2004).
[4] D. C. Look, Mater. Sci. Eng. B **80**, 383 (2001).
[5] D. C. Look and B. Claflin, Phys. Status Solidi B **241**, 624 (2004).
[6] H. S. Bae, C. M. Choi, J. H. Kim, and S. Im, J. Appl. Phys. **97**, 076104 (2005).
[7] E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Gonçalves, A. J. S. Marques, L. M. N. Pereira, R. F. P. Martins, Adv. Mater. **17**, 590 (2005).
[8] Z. Fan, D. Wang, P.-C. Chang, W.-Y. Tseng, and J. G. Lu, Appl. Phys. Lett. **85**, 5923 (2004).
[9] Y. W. Heo, L. C. Tien, Y. Kwon, D. P. Norton, S. J. Pearton, B. S. Kang, F. Ren, Appl. Phys. Lett. **85**, 2274 (2004).
[10] R. L. Hoffman, J. Appl. Phys. **95**, 5813 (2004).
[11] N. W. Emanetoglu, J. Zhu, Y. Chen, J. Zhong, Y. M. Chen, Y. C. Lu, Appl. Phys. Lett. **85**, 3702 (2004).
[12] X. A. Cao and S. D. Arthur, Appl. Phys. Lett. **85**, 3971 (2004).
[13] H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, Appl. Phys. Lett. **77,** 475 (2000).
[14] N. Y. Garces, N. C. Giles, L. E. Halliburton, G. Cantwell, D. B. Eason, D. C. Reynolds, and D. C. Look, Appl. Phys. Lett. **80**, 1334 (2002).
[15] Y. Yan, S. B. Zhang, and S. T. Pantelides, Phys. Rev. Lett. **86**, 5723 (2001).
[16] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[17] J. M. Bian, X. M. Li, C. Y. Zhang, W. D. Yu, and X. D. Gao, Appl. Phys. Lett. **85**, 4070 (2004).

[18] D. C. Look, G. M. Renlund, R. H. Burgener, and J. R. Sizelove, Appl. Phys. Lett. **85**, 5269 (2004).
[19] T. Aoki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).
[20] T. Makino, C. H. Chia, N. T. Tuan, H. D. Sun, Y. Segawa, M. Kawasaki, A. Ohmoto, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 975 (2000).
[21] K. Ip, Y. W. Heo, D. P. Norton, S. J. Pearton, J. R. LaRoche, and F. Ren, Appl. Phys. Lett. **85**, 1169 (2004).
[22] Ya. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, Appl. Phys. Lett. **83**, 4719 (2003).
[23] Ya. I. Alivov, J. E. Van Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, Appl. Phys. Lett. **83**, 2943 (2003).
[24] A. Osinsky, J. W. Dong, M. Z. Kauser, B. Hertog, A. M. Dabiran, P. P. Chow, S. J. Pearton, O. Lopatiuk, and L.Chernyak, Appl. Phys. Lett. **85**, 4272 (2004).
[25] Y. W. Heo, Y. W. Kwon, Y. Li, S. J. Pearton, and D. P. Norton, Appl. Phys. Lett. **84**, 3474 (2004).
[26] H.-K. Kim, S.-H. Han, T.-Y. Seong, and W.-K. Choi, Appl. Phys. Lett. **77**, 1647 (2000).
[27] H. Sheng, N. W. Emanetoglu, S. Muthukumar, S. Feng, and Y. Lu, J. Electron. Mater. **31**, 811 (2002).
[28] S. Y. Kim, H. W. Jang, J. K. Kim, C. M. Jeon, W. I. Park, G.-C. Yi, and J.-L. Lee, J. Electron. Mater. **31**, 868 (2002).
[29] H.-K. Kim, K.-K. Kim, S.-J. Park, T.-Y. Seong, and Y. S. Yoon, Jpn. J. Appl. Phys., Part 2 **41**, L546 (2002).
[30] H. Sheng, N. W. Emanetoglu, S. Muthukumar, B. V. Yakshinskiy, S. Feng, and Y. Lu, J. Electron. Mater. **32**, 935 (2003).
[31] H.-K. Kim, K.-K. Kim, S.-J. Park, T.-Y. Seong, and I. Adesida, J. Appl. Phys., **94**, 4225 (2003).
[32] H.-K. Kim, T.-Y. Seong, K.-K. Kim, S.-J. Park, Y. S. Yoon, and I. Adesida, Jpn. J. Appl. Phys., Part 1 **43**, 976 (2004).
[33] K. Ip, Y. W. Heo, K. H. Baik, D. P. Norton, S. J. Pearton, and F. Ren, Appl. Phys. Lett. **84**, 544 (2004).
[34] S. H. Kim, K. K. Kim, S.-J. Park, and T.-Y. Seong, J. Electrochem. Soc., **152**, G169 (2005).
[35] M. Kurimoto, A. B. M. A. Ashrafi, M. Ebihara, K. Uesugi, H. Kumano, and I. Suemune, Phys. Stat. Sol. (b) **241**, 635, (2004).
[36] S. Kim, B. Kang, F. Ren, Y. Heo, K. Ip, D. P. Norton, and S. J. Pearton, Appl. Phys. Lett. **84**, 1904 (2004).
[37] J. H. Lim, K. K. Kim, D. K. Hwang, H. K. Kim, J. H. Oh, and S. J. Park, J. Electrochem. Soc. **152**, G179 (2005).
[38] H.-K. Kim, S.-H. Han, T.-Y. Seong, and W.-K. Choi, J. Electrochem. Soc., **148**, G114 (2001).
[39] D. R. Lide, CRC Handbook of Chemistry and Physics, 76th ed., Chemical Rubber, Boca Raton, FL (1995).