# Fabrications and Electro-Optical Properties of P-Type ZnO Films


## 彭子安、王立民

E-mail: 9806462@mail.dyu.edu.tw



**ABSTRACT**

In this work, the p-type N-Al co-doped ZnO films were deposited at room temperature on corning glass substrates by magnetron radio frequency (RF) sputtering. We studied the influences of crystalline orientation, surface morphology and doping concentration on the conductivity、carrier concentration、mobility、transmittance and photoluminescence. We realized controllable growth of n-type and p-type Al-N co-doped ZnO thin films by adiusting the radio frequency power, reducing intrinsic defects, and activating N-related acceptors.The sputtering parameters were adjusted and employed to obtain the optimum electro-optical properties of ZnO:(Al, N) thin film.

The optimum conditions for the growth of 400-nm ZnO:(N, Al) films are set with ZnO:Al RF power = 230 W and working pressure = 10 mTorr. The postannealing temperature was fixed in 550 oC for 30 min under nitrogen ambient. As a result, we achieve a lowest resistivity with value of 1.6 Ωcm, carrier concentration of 2.3×1016 m-3 and mobility of 165 cm2/Vs. The average optical transmittance within the visible spectra is more than 80 %. It is found that the ZnO:(Al, N) films with Al/Zn of 10~20 at.% and N/Al of 1~1.3 reveal a p-type character conduction, approaching to the theoretical calculation 2:1.It is also found that the main defects of p-type ZnO:(Al, N) are combined with Zinc vacancies (Vzn) and oxygen vacancies (Vo), possibly leading to the formation of the bonds Al-N by the substitution of Al for of Zn atoms and the substitution of N for O atoms, which may result in p-type conduction in Al-N co-doped ZnO thin films.



Keywords : ZnO、RF magnetron sputtering、resistivity、doping


**Table of Contents**

**REFERENCES**

[1]、K. C. Park, D. Y. Ma, K. H. Kim, “ The physical properties of Al-doped zinc oxide films prepared by RF magnetron sputtering “ , Thin Solid Films 305 (1997) 201-209[2]、J. K. sheu, K. W. Shu, M. L. Lee, C. J. Tun, and G. C. Chi, “ Effect of thermal annealing on Ga-doped ZnO films prepared by magnetron sputtering ” , Journal of The Electrochemical Society. 154 (6) H521-H524 (2007)[3]、J. H. Bae, J. M. Moon, J. W. Kang, H. D. Park, J. J. Kim, W. J. Cho, and H. K. Kima, “ Transparent, Low Resistance, and Flexible Amorphous ZnO-Doped In2O3 Anode Grown on a PES Substrate ” , Journal of The Electrochemical Society, 154 (3) J81-J85 (2007)[4]、楊明輝；工業材料雜誌，第265期2009年1月，P.135[5]、Z. Y. Xiao, Y. C. Liu, R. Mu, D. X. Zhao, and J. Y. Zhang, “ Stability of p-type conductivity in nitrogen-doped ZnO thin ?lm ” , Appl. Phys. Lett. 92, 052106 (2008)[6]、B. Yao, D. Z. Shen, Z. Z. Zhang, X. H. Wang, Z. P. Wei, B. H. Li, Y. M. Lv, and X. W. Fan, “ Effects of nitrogen doping and illumination on lattice constants and conductivity behavior of zinc oxide grown by magnetron sputtering ” , J. Appl. Phys. 99, 123510 (2006)[7]、M. L. Tu, Y. K. Su, C. Y. Ma, “ Nitrogen-doped p-type ZnO ?lms prepared from nitrogen gas radiofrequency magnetron sputtering ” , J. Appl. Phys 100, 053705 (2006)[8]、J. H. Yang, H. S. Kim, J. H. Lim, D. K. Hwang, J. Y. Oh, and S. J. Parkz, “ The Effect of Ar/O2 Sputtering Gas on the Phosphorus-Doped p-Type ZnO Thin Films ” , Journal of The Electrochemical Society, 153 (3) G242-G244 (2006)[9]、K. K. Kim, H. S. Kim, D. K. Hwang, J. H. Lim, and S. J. Park, “ Realization of p-type ZnO thin ?lms via phosphorus doping and thermal activation of the dopant ” , Appl. Phys. Lett., 83, p63-65 (2003)[10]、P. Wang, N. Chen, Z. Yin, F. Yang, C. Peng, R. Dai, and Y. Bai, “ As-doped p-type ZnO ?lms by sputtering and thermal diffusion process ” , J. Appl. Phys. 100, 043704 (2006)[11]、D. K. Hwang, K. H. Bang, M. C. Jeong, J. M. Myoung, “ Effects of RF power variation on properties of ZnO thin ?lms and electrical properties of p – n homojunction ” , J. Crystal Growth 254 (2003) 449 – 455[12]、Y.R. Ryu, S. Zhu, D.C. Look, J.M. Wrobel, H.M. Jeong, H.W. White, “ Synthesis of p-type ZnO films ” , J. Crystal Growth 216 (2000) 330-334[13]、O. Lopatiuk-Tirpak, G. Nootz, E. Flitsiyan, L. Chernyak, L. J. Mandalapu, Z. Yang, J. L. Liu, K. Gartsman, and A. Osinsky, “ In?uence of electron injection on the temporal response of ZnO homojunction photodiodes ” , Appl. Phys. Lett. 91, 042115 (2007)[14]、P. Wanga, N. Chena, Z. Yina, F. Yanga, C. Penga, “ Fabrication and properties of Sb-doped ZnO thin ?lms grown by radio frequency magnetron sputtering ” , J. Crystal Growth 290 (2006) 56 – 60[15]、F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, “ High-mobility Sb-doped p-type ZnO by molecular-beam epitaxy ” , Appl.Phys.Lett. 87, 152101 (2005)[16]、 F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, “ Photoluminescence study of Sb-doped p-type ZnO ?lms by molecular-beam epitaxy ” , Appl. Phys. Lett. 87, 252102 (2005)[17]、S. J. Jiao, Z. Z. Zhang, Y. M. Lu,D. Z. Shen, B. Yao, J. Y. Zhang, B. H. Li, D. X. Zhao, X. W. Fan, and Z. K. Tang,

“ ZnO p-n junction light-emitting diodes fabricated on sapphire substrates ” , Appl. Phys. Lett. 88, 031911 (2006)[18]、S.B. Zhang, S.H. Wei, A. Zunger, "Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO," Phys. Rev. B 63 (2001) 75205.
[19]、Xin-Li Guo, Hitoshi Tabata, and Tomoji Kawai, "Pulsed laser reactive deposition of p-type ZnO film enhanced by an electron cyclotron resonance source ” , J. Cryst. Growth 223,135 (2001)[20]、X. L. Guo , H. Tabata, T. Kawai, “ p-Type conduction in transparent semiconductor ZnO thin ?lms induced by electron cyclotron resonance N2O plasma ” , Optical Materials 19 (2002) 229 – 233[21]、Z. P. Wei, Y. M. Lu, D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Y. Zhang, D. X. Zhao, X. W. Fan, Z. K. “ Tang, Room temperature p-n ZnO blue-violet light-emitting diodes ” , Appl. Phys. Lett. 90, 042113 (2007)[22]、G. W. Cong, W. Q. Peng, H. Y. Wei, X. X. Han, J. J. Wu, X. L. Liu, Q. S. Zhu, Z. G. Wang, J. G. Lu, Z. Z. Ye, L. P. Zhu, H. J. Qian, R. Su, C. H. Hong, J. Zhong, K. Ibrahim, and T. D. Hu, “ Comparison of valence band x-ray photoelectron spectrum between Al – N-codoped and N-doped ZnO ?lms ” , Appl. Phys. Lett. 88, 062110 (2006)[23]、F. Zhuge, L. P. Zhu, Z. Z. Ye, D. W. Ma, J. G. Lu, J. Y. Huang, F. Z. Wang, Z. G. Ji, S. B. Zhang, “ ZnO p-n homojunctions and ohmic contacts to Al – N-co-doped p-type ZnO ” , Appl. Phys. Lett. 87, 092103 (2005)[24]、G. D. Yuan, Z. Z. Ye,L. P. Zhu, Q. Qian, B. H. Zhao, and R. X. Fan, “ Control of conduction type in Al- and N-codoped ZnO thin ?lms ” , Appl. Phys. Lett. 86, 202106 (2005)[25]、J. G. Lu, Z. Z. Ye,F. Zhuge, Y. J. Zeng, B. H. Zhao, and L. P. Zhu, “ p-type conduction in N – Al co-doped ZnO thin ?lms ” , Appl. Phys. Lett., 85, 3134 (2004)[26]、S. Major, Satyendra Kumar, M. Bhatnagar, and K. L. Chopra, “ Effect of hydrogen plasma treatment on transparent conducting oxides ” , Appl. Phys. Lett. 49, 394 (1986).
[27]、S.H.Jeong, J.H.Boo, “ InFluence of target-to-substrate distance on the properties of AZO films grown by RF magnetron sputtering ” , Thin Soild Films 447-448 (2004) 105-110[28]、H. L. Hartnagel, A. K. Jain and C. Jagadish, “ Semiconducting Transparent Thin Films ” , published by Institute of Physics Publication, 1995, Chap. 3.
[29]、B. Lin, Z. Fu, Y. Jia, “ Green luminescent center in undoped zinc oxide ?lms deposited on silicon substrates ” , Appl. Phys. Lett., 79, 943 (2001)[30]、Weitao Caoa, Weimin Du, “ Strong exciton emission from ZnO microcrystal formed by continuous 532 nm laser irradiation ” , Journal of Luminescence 124, 260 – 264 (2007)[31]、I. Hamberg, C. G. Granqvist, K. -F. Berggren, B. E. Sernelius, and L. Engstr?m, “ Band-gap widening in heavily Sn-doped In2O3 ” , Phys. Rev. B 30, 3240 - 3249 (1984)[32]、Jianguo Lu, Qunian Liang, Yinzhu Zhang1, Zhizhen Ye ,and Shizuo Fujita, “ Improved p-type conductivity and acceptor states in N-doped ZnO thin ?lms ” , J. Phys. D: Appl. Phys., 40, 3177 – 3181 (2007)[33]、Day-Shan Liua, Chia-Sheng Sheu, Ching-Ting Lee, “ Aluminum-nitride codoped zinc oxide ?lms prepared using a radio-frequency magnetron cosputtering system ” , J. Appl. Phys. 102, 033516 (2007)[34]、Z. Z. Ye, J. G. Lu, Y. Z. Zhang, Y. J. Zeng, L. L. Chen, F. Zhuge, G. D. Yuan, H. P. He, L. P. Zhu, J. Y. Huang, and B. H. Zhao, “ ZnO light-emitting diodes fabricated on Si substrates with homobuffer layers ” , Appl. Phys. Lett. 91, 113503 (2007)[35]、J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood, (1971)[36]、Zhang Xiaodan, Fan Hongbing, Zhao Ying, Sun Jian, Wei Changchun, Zhang Cunshan, Wei Changchun, Zhang Cunshan, “ Fabrication of high hole-carrier density p-type ZnO thin ?lms by N – Al co-doping ” , Applied Surface Science 253 (2007) 3825 – 3827[37]、S. King, J.G.E. Gardeniers, I.W. Boyd, Appl. Surf. Sci. 96 – 98 (1996) 811[38]、Xuemei Teng, Hongtao Fan, Shusheng Pan, Cong Ye, Guanghai Li, “ Abnormal photoluminescence of ZnO thin film on ITO glass ” , Materials Letters 61 (2007) 201 – 204[39]、Zeng Y J, Ye Z Z, Xu W Z, Lu J G, He H P, Zhu L P, Zhao B H, Che Y and Zhang S B, “ p-type behavior in nominally undoped ZnO thin films by oxygen plasma growth ” , Appl. Phys. Lett. 88 262103 (2006)[40]、K. Minegish, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga, A. Shimizu, “ Growth of p-type Zinc Oxide Films by Chemical Vapor Deposition ” , Jpn J. Appl. Phys. 36 (1997) L1453.
[41]、T. Yamamoto, “ Codoping for the fabrication of p-type ZnO ” , Thin Solid Film 420 (2002) 100.
[42]、T. Yamamoto, “ Codoping method for solutions of doping problems in wide-band-gap semiconductors ” , Phys. Stat. Sol. (a) 193 (3) (2002) 423.
[43]、F.Shinoki and A.Itoh, “ Mechanism of rf reactive sputtering ” , J.Appl.Phys., 45(1975), 3381-3384[44]、Zhi-zhen Ye, Qing Qian, Guo-Dong Yuan, Bing-Hui Zhao, De-Wei Ma, “ Effect of oxygen partial pressure ratios on the properties of Al – N co-doped ZnO thin ?lms ” , Journal of Crystal Growth 274 (2005) 178 – 182[45]、D. C. Look and D. C. Reynolds, “ Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy ” , Appl. Phys. Lett., Vol. 81, No. 10, 2 September 2002[46]、B. Chapman, “ Glow Discharge Processes ” , John Wiley & Sonc. Inc., N.Y.,(1980)[47]、T.L.Tansley, D.F.Neely, “ Adsorption, desorption and conductivity of sputtered zinc oxide thin films ” , Thin Soild Films 121 (1984) 95[48]、G. Sanon, R. Rup, A. Mansingh, “ Growth and characterization of tin oxide films prepared by chemical vapour deposition ” , Thin Solid Films, 190 (1990) 287.
[49]、Su-Shia Lin, Jow-Lay Huang, Ding Fwu Lii, “ The effects of r.f. power and substrate temperature on the properties of ZnO films ” , Surface and Coatings Technology 176 (2004) 173-181[50]、W. Tang, D. C. Cameron, “ Aluminum-doped zinc oxide transparent conductors deposited by the sol-gel process ” , Thin Solid Films 238 (1994) 83[51]、Y. Igasaki and H. Saito, “ The effects of zinc diffusion on the electrical and optical properties of ZnO:Al films prepared by r.f. reactive sputtering ” , Thin Solid Films 199 (1991) 223[52]、S. Naguchi and H. Sakata, “ Electrical properties of undoped In2O3 films prepared by reactive evaporation ” , J. Phys. D, 13 (1980) 1129[53]、J. Bardeen, W. Shockley, Phys. Rev. 80 (1950) 72.
[54]、B.K. Ridley, J. Phys. C 10 (1977) 1589.
[55]、J.Y.W. Seto, J. Appl. Phys. 46 (1975) 5247.
[56]、N.F. Mott, J. Non-Cryst. Solids 1 (1968) 1.
[57]、R.M. Hill, Phil. Mag. 24 (1971) 1307.

[58]、H. X. Jiang and J.Y. Lin, Phys. Rev. B. 15(1989) 40.
[59]、H. X. Jiang, G. Brown, and J. Y. Lin, “ Persistent photoconductivity in II-VI and III-V semiconductor alloys and a novel infrared detector ”, J. Appl. Phys. 9. (1991) 69[60]、C. W. Su, M. S. Huang, Y. C. Chang, T. h. Tsai, Y. h. Lee, and J. C. Lee, “ Determination of composition in stoichiometric Co-N ultrathin films by nitrogen plasma sputtering ”, JAP 105, 033509 (2009)[61]、T. Yamamoto, “ Codoping for the fabrication of p-type ZnO ”, Thin Solid Films , 420-421 (2002) 100-106[62]、T.Yamamoto, “ Control of N-Impurity States in N-Doped ZnO, ZnS and ZnTe ”, Jpn. J. Appl. Phys. 42 (2003) p.L414-L516