

P型氧化鋅薄膜之製作與光電特性研究

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摘要

在本研究裡利用RF濺鍍成長ZnO:(Al, N)薄膜，探討ZnO:(Al, N)薄膜的結構、表面形貌、摻雜比例對於導電性(conductivity)、載子濃度(carrier concentration)、遷移率(mobility)、光穿透率(transmission)以及光激發螢光發光(Photoluminescence)之影響，本研究透過射頻功率的調變、降低本質缺陷、活化受體，實現可控制生長n型與p型的氧化鋅薄膜。進而獲得具良好光電特性ZnO:(Al, N)薄膜之最佳製程條件。

實驗結果顯示最佳製程條件為ZnO:Al靶材射頻功率230 W、工作壓力10 mTorr、工作溫度室溫環境下，薄膜厚度維持在400 nm。ZnO:(Al, N)薄膜其電阻率1.6 ? cm、載子濃度 2.32×10^{16} cm⁻³、載子遷移率 165 cm²/V·s，在可見光範圍之穿透率平均可以達到80%。我們發現ZnO : (Al, N)薄膜摻雜原子的比率在Al/Zn為10~20%與N/Al為1~1.3時，是適合成長出p型ZnO: (N, Al)薄膜的條件，此結果非常接近理論值N/Al=2:1。分析發現p型ZnO:(Al, N)薄膜，主要以氧空缺與鋅空缺存在。同時也提供氮原子取代氧空缺與鋁原子取代鋅空缺的機會，製程p型ZnO:(Al, N)薄膜機會也大幅增加。

關鍵詞：氧化鋅、射頻磁控濺鍍法、電阻率、摻雜

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參考文獻

- [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 ?lms ” , 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. Flitsiany, L. Chernyak, L. J. Mandalapu, Z. Yang, J. L. Liu, K. Gartsman, and A. Osinsky, “ Influence 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. Minegishi, 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 & Sons. 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

