

Synthesis and Characterization of Al-Doped ZnO Thin Films by Sol-Gel Method

林育玄、林志哲；姚品全

E-mail: 9806424@mail.dyu.edu.tw

ABSTRACT

In this study focus on sol-gel method, the adjustment of pH by adding inorganic aluminum salts, synthesis and stability of colloidal liquid coating. Deposition by spin-coating on the glass substrate, in the appropriate heating treatment, crystalline form of aluminum-doped zinc oxide films (ZnO: Al, AZO), When the 3:1 ratio of zinc and citric acid, aluminum-doped to 2.25 when the volume of the AZO thin film synthesis, of AZO film was as low as 9.96×10^{-3} μm after annealing in Ar at 700°C and heat treatment with hydrogen at 700°C. Shows the XRD diffraction in the vicinity of $2\theta = 34^\circ$ with (002) crystal face of the preferred orientation, And non-metallic state of the crystallization of zinc or aluminum there, Visible region (400 ~ 800nm) transmittance of up to 88 ~ 93%, And the use of Hall effect show that mobility of $5.03\text{cm}^2/\text{Vs}$ and carrier concentration of $1.25 \times 10^{20}\text{cm}^{-3}$, AZO motor show, the carrier concentration, mobility and resistivity changes between the ion scattering by impurities and grain boundary scattering to explain.

This sol-gel coating solution can be carried out under room temperature operation, as compared to conventional vacuum film-forming systems, more economical process to reduce the cost of the use of special solvents. This study focused on the process parameters, including the synthesis of system pH, heat treatment temperature and atmosphere conditions on the AZO thin films, such as electrical and optical properties of the impact.

Heat treatment, the only access to the formation of a small amount of hydrogen can be better transmittance of the thin film, optical energy gap with the carrier to upgrade and increase concentration, this is the phenomenon of Burstein-Moss effect, showed an increase after the aluminum-doped sub-set of the occupied conduction band at the bottom of the original ZnO caused by the effect.

Keywords : Aluminum-doped zinc oxide (AZO)、sol - gel method (sol-gel)、nano-thin film、after、pH

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REFERENCES

- [1]陳光華, 奈米薄膜技術與應用, 五南圖書出版(2005)[2]馬遠榮, “奈米科技”, 周商出版 (2002)[3]王崇人, “神奇奈米科學”, 科學發展月刊, 354, 49 (2002)[4]盧永坤, 奈米科技概論, 滄海書局(民94)[5]范光照, 奈米工程概論, 普林斯頓出版(民92)[6]馬振基, “奈米材料科技原理與應用”, 全華科技圖書 (2003)[7]K. L. Chopra, S. Magor and D. K. Pandya, Thin Solid Films, 102,1(1983)[8]許國銓, “科技玻璃-高性能透明導電玻璃”, 材料與社會, 84,110-119 (1993)[9]D.S. Ginley and C. Bright, MRS Bull., Aug., 15 (2000)[10]B.G. Lewis and D.C. Paine, MRS Bull., Aug., 22 (2000)[11]T. Minami, H.Sato, H.Imamoto and S.Takata, "Substrate temperature dependence of transparent conducting Al-doped ZnO thin films prepared by magnetron sputtering",Jan.J.Appl.Phys.,31(1992) pp.253.
- [12]H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, MRS Bull., Aug.

- [13]R. G. Gordon, MRS Bull., Aug., 52 (2000)[14]T. Minami, MRS Bull., Aug., 38 (2000)[15]A.J. Freeman, K.R. Poeppelmeier, T.O. Mason, R.P.H. Chang, and T.J. Marks, MRS Bull., Aug., 45 (2000).
- [16]R. G. Gordon, MRS Bull., Aug., 52 (2000)[17]T. J. Coutts, D. L. Young, and X. Li, MRS Bull., Aug.,58 (2000)[18]T.O. Mason, R.P.H. Chang, T.J. Mark, and K.R. Poeppelmeier, “ ImprovedTransparent Conducting Oxides for Photovoltaics ” , Final Research Report,Northwestern University, Evanston, Illinois, (1 may 1999-31 Dec. 2002)[19]CHEN JianLin, CHEN Ding Sci China Ser E-Tech Sci | Jan. 2009 | vol. 52 | no. 1 | 88-94[20]賴明雄、溫志中, 工業材料, 179, 145 (1999)[21]黃智偉, “ 銀奈米粒子之製備及其在高分子微球上之被覆研究 ” , 國立成功大學化學工程研究所碩士論文 (2004)[22]Graffet, E., Tchikart, M., Elkedim, O. and Rahouadj, R., Mater Charact.,36, 185 (1996)[23]Amulyavichus, A., Daugvila, A., Davidonis, R. and Sipavichus,C.Fiz. Met. Metalloved., 85, 111 (1998).
- [24]T. Minami, H. Nanto, S. Shoji, and S. Takata, Jpn. J. Appl. Phys.Part2, 23, L280 (1984)[25]J. H. Lee and B. O. Park, Thin Solid Film, 426, 94 (2003)[26]A.J. Freeman, K.R. Poeppelmeier, T.O. Mason, R.P.H. Chang, and T.J. Marks, MRS Bull., Aug., 45 (2000).
- [27]T.O. Mason, R.P.H. Chang, T.J. Mark, and K.R. Poeppelmeier, “ ImprovedTransparent Conducting Oxides for Photovoltaics ” , Final Research Report,Northwestern University, Evanston, Illinois, (1 may 1999-31 Dec. 2002)[28]楊明輝, 工業材料, 179, 134 (1999)[29]M.-M. Bagheri-Mohagheghi and M. Shokoo-Saremi, Semicond.Sci. Technol., 18, 97 (2003)[30]D. Song, J. Xia, E.-C. Cho, and A. G. Aberie, PhotovoltaicsSpecialResearch Centre, University of New South Wales, UNSW SydneyNSW 2052, Australia[31]G. B. Palmer, K.R. Poeppelmeier, and T. O. Mason, Chem. Mater9,3121 (1997)[32]A. Wang, J. R. Babcock, N. L. Edleman, A. W. Metz, M. A. Lane, R.Asahi, V. P. Dravid, C. R. Kannewurf, A. J. Freeman, and T. J.Marks,PNAS, 98(13), 7113 (2001)[33] “ sol-gel technologies and their products ” , <http://www.chemat.com/>,CHEMAT Technology, Inc.溶膠-凝膠之形成與應用[34]謝坤龍, “ 鈹銀合金/氧化鋁複合膜之特性研究:/以溶膠凝膠法修飾基材孔徑之探討 ” , 國立成功大學化學工程研究所碩士論文 (2000)[35]R.W Jones, Fundamental principles of sol-gel technology,The institute of metals(1989)[36]S.Sakka and K.Kamiya, ‘ Glasses from metal alcoholates ’ , J.Non-Cryst.Solid,42,(1980)40[37]K.Kamiya,K.Tanimoto and T.Yoko, ‘ Presparation of Tio2 fibersby hydrolysis and polycondensation of Ti(O-i-C3H7)4 ’ ,J.Mater. Sci.Lett,5,(1986)402[38]K. L. Chopra, S. Magor and D. K. Pandya, Thin Solid Films, 102, 1(1983)[39]H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagadish, “ Semiconducting Transparent Thin Films ” , Institute of PhysicsPublishing (1995)[40]李玉華, “ 透明導電膜及其應用 ” , 科儀新知, 12, 94 (1990)[41]H. L. Hartnagel, A. L. Dawar,A. K. Jain, C. Jagadish, “ Semiconducting Transparent Thin Films ” ,Institute of Physics Publishing (1995)[42]M. T. Young and S. D. Keun, Thin Solid Films, vol. 410, pp. 8, 2002.
- [43]J. Hu and R. G. Gorden, J. Appl. Phys., vol. 71, pp. 880, 1992.
- [44]F. Furusaki, J. Takahashi and K. Kodaira, J. of the Japan CeramicSociety, vol. 102, pp. 200, 1994.
- [45]M. S. Wu, A. Azuma, T. Shiosaki and A. Kawabata, IEEE Transactions on Ultrasonics, Ferroelectrics, and FrequencyControl, vol. 36, n 4, Jul, p 442-445, 1989.
- [46]W. Water and S. Y. Chu, Materials Letters, vol. 55, pp. 67, 2002.
- [47]Y. Yoshino, T. Makino, Y. Katayama and T. Hata, Vacuum, vol.59, pp. 538, 2000 .
- [48]Y. Igasaki and H. Saito, Thin Solid Films, vol. 199, pp. 223, 1991.
- [49]H. S. Randhawa, M. D. Matthews and R. F. Bunshan, Thin Solid Films, vol. 83, pp. 267, 1981.
- [50]E. S Shim et al., Appl. Surf. Sci. , vol. 186, 474, 2002.
- [51]J. L. Vossen, “ Transparent Conducting Films ” , Physics of Thin Films, 1977[52]J.H.Lee and B.O Park,Thin Solid Film,426,94(2003)[53]T. Tsuchiya,T.Enomoto,and T.sei,J Non-Cryst.Solids, 178,327 (1994)[54]Y.Ohya,H.Saiki,and Y.Takahashi,J.Mater.Sci,29,4099(1994)[55]W.Tangand D.C.Cameron,Thin Solid Films,238,83(1994)[56]Y.Ohya,H.Saiki,T Tanaka,and Y.Takahashi, J.Am.Ceram. Soc,79852(1996)[57]K. L. Chopra, S. Magor and D. K. Pandya, Thin Solid Films, 102,1(1983)[58]H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagadish, “ Semiconducting Transparent Thin Films ” , Institute of PhysicsPublishing (1995)[59]莊萬發, “ 超微粒子理論應用 ” , 臺南:復漢 (1995)。
- [60]K Ellmer, J. Phys. D: Appl. Phys, vol. 34 pp. 3097 – 3108, 2001.
- [61]D. MONDELAERS G. VANHOYLAND Journal of Sol-Gel Science and Technology 26, 523 – 526, 2003