

Deposition of Al-doped Zn films by magnetron sputtering and its application in dye-sensitized solar cells

區佳揚、姚品全、施能夫

E-mail: 322106@mail.dyu.edu.tw

ABSTRACT

In this study, deposition of Al-doped ZnO(AZO) films by magnetron sputtering system, and applied to dye sensitized solar cells (DSSC). It can be divided into two parts. The first part is mainly to explore the process parameters of magnetron sputtering system to deposit AZO thin film. Using FE-SEM, XRD, Hall-effect, UV-VIS to analyze the optical and electrical properties of AZO thin films. The experimental results show: when working pressure in 2×10^{-3} torr, subtract temperature in 325 °C, the resistivity is 2.9401×10^{-4} (Ω · cm), and concentration is 3.2599×10^{21} (cm⁻³), and mobility is 6.4682 (cm² · V⁻¹ · S⁻¹). It can further enhance the electric conductivity of AZO, when it in 550 °C under an Ar/H₂ (6%) atmosphere of annealing for one hour. The resistivity is 2.0176×10^{-4} (Ω · cm), and concentration is 2.7939×10^{21} (cm⁻³), and mobility is 11.08518 (cm² · V⁻¹ · S⁻¹). After deposited AZO thin films, we use hydrochloric acid to etch the surface of AZO thin films. Using UV-VIS, Four-Point Probe, Haze meter, FE-SEM, to analyze the electrical and optical properties of AZO thin films. The second part, we use AZO transparent conductive glass substrate in the first part, and it will be applying to DSSC. Using Degussa P25 TiO₂ to spin coating(8.6 μm) under AZO thin film for the photo-electrode, then we sinter the photo-electrode in 450 °C. Our DSSC uses D719 dyes, EL-100 electrolytes and Pt counter-electrode. We measured the photovoltaic conversion efficiency(simulated AM 1.5 sunlight), and the result shows: $V_{oc}=0.8519$ V, $J_{sc}=4.460$ mA/cm², $FF=0.53$, $\eta=2.009\%$.

Keywords : magnetron sputtering system、AZO、Dye-Sensitized Solar Cell

Table of Contents

封面內頁 簽名頁 授權書.....	iii	中文摘要.....	iv	Abstract.....	vi	誌謝.....	vii	目錄.....	1
1.2研究動機.....	2	1.3論文架構.....	4	第二章 文獻回顧與理論原理.....	5	2.1透明導電薄膜.....	5	1.1.1前言.....	1
5 2.1.1透明導電膜概論.....	5	5 2.1.2氧化鋅(ZnO)性質.....	8	2.1.3透明導電膜導電因素.....	8	2.2太陽電池簡介.....	15	2.3 DSSC之工作原理.....	15
11 2.1.4透明導電薄膜光學特性.....	13	13 2.2太陽電池簡介.....	15	15 2.3 DSSC之工作原理.....	15	16 2.4 DSSC之組成結構.....	18	18 2.4.1透明導電玻璃.....	19
19 2.4.3染料.....	21	18 2.4.4電解質.....	23	19 2.4.2 TiO ₂ 光電極.....	25	19 2.4.3染料.....	21	21 2.4.4電解質.....	23
28 3.3實驗流程.....	29	21 2.4.4電解質.....	23	23 2.4.5對電極.....	25	25 2.5濺鍍原理.....	25	23 2.4.5對電極.....	25
AZO表面粗糙化處理.....	32	29 3.4濺鍍AZO薄膜.....	29	29 3.5熱退火處理.....	31	31 3.6	31	32 3.7 DSSC製作步驟.....	32
DSSC光電極製備.....	33	32 3.7.1 P25-TiO ₂ 漿料配製.....	32	32 3.7.2	32	34 3.7.3染料.....	34	34 3.7.4電解液.....	34
34 3.7.6元件組裝.....	35	34 3.7.5對電極製作.....	34	34 3.7.6元件組裝.....	35	35 3.8儀器量測分析.....	36	36 3.8.1 UV-VIS光譜儀.....	36
36 3.8.2霍爾量測系統.....	37	36 3.8.2霍爾量測系統.....	37	37 3.8.3 X光繞射儀.....	38	37 3.8.3 X光繞射儀.....	37	38 3.8.4場發射掃描式電子顯微鏡.....	38
39 3.8.5標準太陽光源模擬系統.....	39	39 3.8.5標準太陽光源模擬系統.....	39	40 第四章 結果與討論.....	41	41 4.1 AZO薄膜特性分析.....	41	41 4.2退火溫度對AZO薄膜之影響.....	41
41 4.2基板溫度對AZO薄膜之影響.....	41	41 4.2基板溫度對AZO薄膜之影響.....	41	41 4.3退火溫度對AZO薄膜之影響.....	41	41 4.3退火溫度對AZO薄膜之影響.....	41	42 4.4退火溫度對DSSC之影響.....	42
AZO表面粗糙化處理.....	51	42 4.4退火溫度對DSSC之影響.....	51	42 4.5 DSSC製程與分析.....	51	42 4.5 DSSC製程與分析.....	51	43 4.6燒結溫度對DSSC之影響.....	43
4.7 TiO ₂ 膜厚對DSSC之影響.....	66	43 4.6燒結溫度對DSSC之影響.....	66	43 4.7 TiO ₂ 膜厚對DSSC之影響.....	66	44 4.8熱退火處理對光電極之影響.....	68	44 第五章 結論與建議.....	68
71 5.1結論.....	71	44 4.8熱退火處理對光電極之影響.....	68	71 5.2建議.....	71	72 參考文獻.....	72	73 圖目錄	73
9 圖2-2 Burstein-Moss shift.....	14	73 圖目錄	73	72 參考文獻.....	72	圖2-1 ZnO結構圖.....	9	圖2-2 Burstein-Moss shift.....	14
18 圖2-5染料敏化太陽能電池的基本架構.....	18	圖2-1 ZnO結構圖.....	9	圖2-3 DSSC之工作原理.....	14	圖2-3 DSSC之工作原理.....	14	圖2-3 DSSC之工作原理.....	14
18 圖2-6各種氧化物半導體的能階示意圖.....	18	圖2-3 DSSC之工作原理.....	14	17 圖2-4 TiO ₂ /染料/電解質之電子能階圖.....	17	圖2-4 TiO ₂ /染料/電解質之電子能階圖.....	17	圖2-4 TiO ₂ /染料/電解質之電子能階圖.....	17
21 圖3-1磁控濺鍍系統.....	30	17 圖2-4 TiO ₂ /染料/電解質之電子能階圖.....	17	30 圖3-2高溫爐管示意圖.....	31	31 圖3-3光電極製作流程.....	31	30 圖3-2高溫爐管示意圖.....	30
33 圖3-4 DSSC元件組裝圖.....	35	31 圖3-3光電極製作流程.....	31	35 圖3-5 UV-VIS-NIR光譜分析儀.....	36	36 圖3-6霍爾量測系統.....	36	35 圖3-5 UV-VIS-NIR光譜分析儀.....	35
37 圖3-7 X光繞射儀.....	38	36 圖3-6霍爾量測系統.....	36	38 圖3-8場發射掃描式電子顯微鏡.....	39	39 圖3-9標準太陽光源模擬系統.....	39	38 圖3-8場發射掃描式電子顯微鏡.....	38
40 圖4-1不同基板溫度下之AZO薄膜UV-VIS光譜圖.....	42	39 圖3-9標準太陽光源模擬系統.....	39	42 圖4-2不同基板溫度下之AZO薄膜電性.....	42	42 圖4-2不同基板溫度下之AZO薄膜電性.....	42	43 圖4-3不同基板溫度下之AZO薄膜XRD.....	44
43 圖4-3不同基板溫度下之AZO薄膜XRD.....	44	44 圖4-4不同基板溫度下XRD繞射峰所量得之FWHM.....	45	44 圖4-4不同基板溫度下XRD繞射峰所量得之FWHM.....	45	45 圖4-5不同基板溫度下之AZO薄膜Grain size.....	45	45 圖4-6不同退火溫度下之AZO薄膜Grain size.....	45

之AZO薄膜UV-VIS光譜圖.....	47	圖4-7不同退火溫度下之AZO薄膜電性.....	48	圖4-8不同退火溫度下之AZO薄膜XRD.....	49	圖4-9不同退火溫度下XRD繞射峰所量得之FWHM.....	49	圖4-10不同退火溫度下之AZO薄膜Grain size.....	50	圖4-11 HCl(0.025M)蝕刻AZO薄膜之UV-VIS光譜圖.....	52	圖4-12 HCl(0.05M)蝕刻AZO薄膜之UV-VIS光譜圖.....	53	圖4-13 HCl(0.075M)蝕刻AZO薄膜之UV-VIS光譜圖.....	54	圖4-14 HCl(0.1M)蝕刻AZO薄膜之UV-VIS光譜圖.....	55	圖4-15 HCl(0.025M)蝕刻AZO薄膜之SEM剖面、正面圖.....	56	圖4-16 HCl(0.05M)蝕刻AZO薄膜之SEM剖面、正面圖.....	57	圖4-17 HCl(0.075M)蝕刻AZO薄膜之SEM剖面、正面圖.....	58	圖4-18 HCl(0.1M)蝕刻AZO薄膜之SEM剖面、正面圖.....	59	圖4-19 Degussa P25 TiO ₂ 膜厚圖.....	61	圖4-20 Degussa P25 TiO ₂ 之表面形貌.....	62	圖4-21光電極不同燒結溫度之DSSC I-V圖.....	64	圖4-22光電極不同燒結溫度之AZO電阻率.....	65	圖4-23光電極450 不同TiO ₂ 膜厚之DSSC I-V圖.....	67	圖4-24光電極不同退火溫度之AZO電阻率.....	69	圖4-25光電極不同退火溫度之DSSC I-V圖.....	70	表目錄 表1-1 2008年各式太陽能電池轉換效率.....	3	表2-1透明導電膜的應用.....	7	表2-2常見的TCO薄膜製備方法.....	8	表2-3氧化鋅的基本特性.....	10	表4-1不同基板溫度下之AZO薄膜電性表.....	43	表4-2不同退火溫度下之AZO薄膜電性表.....	48	表4-3 HCl(0.025M)蝕刻AZO薄膜之光電特性.....	52	表4-4 HCl(0.05M)蝕刻AZO薄膜之光電特性.....	53	表4-5 HCl(0.075M)蝕刻AZO薄膜之光電特性.....	54	表4-6 HCl(0.1M)蝕刻AZO薄膜之光電特性.....	55	表4-7光電極不同燒結溫度之DSSC I-V表現.....	64	表4-8光電極不同TiO ₂ 膜厚之DSSC I-V表現.....	67	表4-9光電極不同退火溫度之DSSC I-V表現.....	70
----------------------	----	--------------------------	----	---------------------------	----	--------------------------------	----	-----------------------------------	----	---	----	--	----	---	----	---------------------------------------	----	---	----	--	----	---	----	---------------------------------------	----	---	----	---	----	-------------------------------	----	----------------------------	----	--	----	----------------------------	----	-------------------------------	----	--------------------------------	---	-------------------	---	-----------------------	---	-------------------	----	---------------------------	----	---------------------------	----	-----------------------------------	----	----------------------------------	----	-----------------------------------	----	---------------------------------	----	-------------------------------	----	--	----	-------------------------------	----

REFERENCES

- [1] M.Gratzel, " Powering the planet ", Nature , vol.403, p.363, 2000.
- [2] Martin A. Green1, Keith Emery, Yoshihiro Hishikawa and Wilhelm Warta, " Short communication Solar Cell Efficiency Tables (Version 31) ", Prog. Photovolt: Res. Appl. , vol.16, p.61-67, 2008.
- [3] T. Miyasaka, M. Ikegami and Y. Kijitora, " Photovoltaic Performance of Plastic Dye-Sensitized Electrodes Prepared by Low-Temperature Binder-Free Coating of Mesoscopic Titania " Journal of The Electrochemical Society, vol.154, p.A455-A461, 2007.
- [4] T.O. Mason, R.P.H. Chang, T.J. Mark, and K.R. Poeppelmeier, " Improved Transparent Conducting Oxides for Photovoltaics " , Final Research Report,Northwestern University, Evanston, Illinois, 1 may 1999-31 Dec. 2002.
- [5] 楊明輝 , 工業材料 , 179 , 134, 1999.
- [6] D. Song, J. Xia, E.-C. Cho, and A. G. Aberie, " Photovoltaics SpecialResearch Centre " , University of New South Wales, UNSW SydneyNSW 2052, Australia [7] 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, vol.98, p.7113-7116, 2001.
- [8] 曲喜新、楊邦朝、姜節儉、張懷武編著 , “電子薄膜材料 ” , 北京科學出版社出版 , p93, 1996.
- [9] H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, " Semiconducting Transparent Thin Films " , Institute of Physics Publishing, 1995.
- [10] 李玉華 , “透明導電膜及其應用 ” , 科儀新知 , 第十二卷第一期 , p94-102, 1990.
- [11] J. L. Vossen, " Transparent Conducting Films " , Physics of Thin Film, vol.9, p1-64, 1977.
- [12] A. Suzuki, T. Matsushita, T. Aoki, A. Mori, M. Okuda, " Highly conducting transparent indium tin oxide films prepared by pulsed laser deposition " , Thin Solid Films, vol.411, p23-27, 2002.
- [13] T. Minami, " Transparent conducting oxide semiconductors for transparent electrodes " , Semiconductor Science Technology, vol.20, p.35-44, 2005.
- [14] B. G. Lewis and D. C. Paine, " Applications and Processing of Transparent Conducting Oxides " , MRS Bulletin, vol. 25, p.22-27, 2000.
- [15] R. Wendt, K. Ellmer, K. Wiesemann, " Thermal power at a substrate during ZnO:Al thin film deposition in a planar magnetron sputtering system " , Journal of Applied. Physics, vol.82, p.2115-2122, 1997.
- [16] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wenisch, and T. Yao, " Ga-doped ZnO films grown on GaN templates by plasma-assisted molecular-beam epitaxy " , Applied Physics Letters.,vol.77, p.3761-3763, 2000.
- [17] V. Assuncao, E. Fortunato, A. Marques, A. Goncalves, I. Ferreira, H. Aguas, R. Martins, " New challenges on gallium-doped zinc oxide films prepared by r.f. magnetron sputtering " , Thin Solid Films, vol.442, p.102-106, 2003.
- [18] 林素霞 , 博士論文 , “氧化鋅薄膜特性改良與應用 ” , 國立成功大學材料科學研究所, 2003.
- [19] P. Nunes, E. Fortunato, R. Martins, " Influence of the annealing conditions on the properties of ZnO thin films " , The International Journal of Inorganic Materials, vol.3, No.8, p.1125-1128, 2001.
- [20] T. Minami, S. Suzuki, T. Miyata, " Electrical Conduction Mechanism of Highly Transparent and Conductive ZnO Thin Films " , MRS Symp. Proc, vol.666, 2001.
- [21] T. Minami, " New n-type transparent conducting oxides " , MRS Bulletin, Aug. 2000.
- [22] C. Agashe, O. Kluth, J. Hu"pkes, U. Zastrow, B. Rech, M. Wuttig, " Efforts to improve carrier mobility in radio frequency sputtered

- aluminum doped zinc oxide films ” , J. Appl. Phys., vol.95, p.1911-1917, 2004.
- [23] 潘漢昌、蕭銘華、蘇健穎、蕭健男， “ 透明導電膜簡介 ” ，科儀新知 , 26 , 46,2004.
- [24] 陳建華 , “ P-型透明導電膜應用於有機發光二極體 ” , 國立成功大學化學工程研究所碩士論文, 2003.
- [25] U". O"zgu"r, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reschikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoc,, “ A comprehensive review of ZnO materials and devices ” , J. Appl. Phys., 98, 041301, 2005.
- [26] J. H. Lee and B. O. Park, “ Transparent conducting ZnO:Al, In and Sn thin films deposited by the sol – gel method ” , Thin Solid Films, Vol. 426, p.94-99, 2003.
- [27] S. Y. Lee and B. O. Park, “ Electrical and optical properties of In₂O₃ – ZnO thin films prepared by sol – gel method ” , Thin Solid Films, vol.484, p.184-187, 2005.
- [28] 楊明輝 , 透明導電薄膜 , 藝軒圖書 [29] H.W. Lee, S.P. Lau,, Y.G. Wang, K.Y. Tse, H.H. Hng, B.K. Tay, J. Cryst. Growth, vol.268, p.596-601 ,2004.
- [30] Z. C. Zin, I. Hamberg, and C.G. Granqvist, “ Optical properties of sputter-deposited ZnO:Al thin films ” , J. Appl. Phys., 64, 5117, 1988.
- [31] T. Minami, H. Nanto, and S. Takata, ” Optical properties of aluminum doped zinc oxide thin films prepared by RF magnetron sputtering ” , Jpn. J. Appl. Phys, 24, p.L605-L607, 1985.
- [32] Dieter K. Schroder, “ Semiconductor material and device characterization ” , A Wiley-Interscience Publication , 1998.
- [33] Frank Hurd and Robert Livingston , “ The Quantum Yields of some Dye-sensitized Photooxidations ” , J. Phys. Chem. , 44 , 865, 1940.
- [34] S. Chaberek, A. Shepp and R. J. Allen , “ Dye-Sensitized Photopolymerization Processes.1a I. The Thionine-Nitrilotripropionamide-Acrylamide System1b ” , J. Phys. Chem. , 69 , 641-647, 1965.
- [35] S. Chaberek, A. Shepp and R. J. Allen , “ Dye-Sensitized Photopolymerization Processes.1a III. The Photoreducing Activity of Some Dicarbonyl Compounds ” , J. Phys. Chem. , 69 , 2834, 1965.
- [36] Kearns et al. , J. Am. Chem. Soc. , 89 , 5456, 1967.
- [37] H. Tsubomura, M. Matsumura, Y. Nomura and T. Amamiya, “ Dye-sensitized zinc oxide/aqueous electrolyte/platinum photocell ” , Nature, 261, 402, 1976 [38] B. O ' Regan and M. Gratzel , “ A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films ” , Nature, vol. 353 , p.737-740, 1991.
- [39] M. Gratzel, “ Photoelectrochemical cells, ” Nature, vol.414, p. 338-344, 2001.
- [40] A. Zaban, S. Ferrere, B. A. Gregg, J. Phys. Chem. B, 102, 452, 1998.
- [41] K. Kalyanasundaram, M. Gratzel, “ Applications of functionalized transition metal complexes in photonic and optoelectronic devices ” , Coordination Chemistry Reviews, vol.77, p.347-414, 1998.
- [42] 劉茂煌,奈米光電池,工業材料雜誌203期,P93.
- [43] K. Kalyanasundaram and M. Gratzel, “ Applications of functionalized transition metal complexes in photonic and optoelectronic devices, ” Coordin. Chem. Rev, vol.77, p.347 – 414, 1998.
- [44] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, “ Dye-sensitized nanocrystalline TiO₂ solar cells based on novel coumarin dyes, ” Sol. Energy Mater. Sol. Cells, vol.77, p.89, 2003.
- [45] T. Horiuchi, H. Miura, S. Uchida, “ Highly-efficient metal-free organic dyes for dye-sensitized solar cells ” , Chem. Commun, p. 3036, 2003.
- [46] 董永樸,釤金屬染料在染料敏化太陽電池的演進,工業材料雜誌255期,p.110.
- [47] 蔡松雨,染料敏化太陽電池技術介紹,工業材料雜誌241 期, p.107 , 96年1月.
- [48] G. Schlichth0rl, S. Y. Huang, J. Sprague, and A. J. Frank, “ Band edge movement and recombination kinetics in dye-sensitized nanocrystalline TiO₂ solar cells: a study by intensity modulated photovoltage spectroscopy, ” J. Phys. Chem B, vol.101, p.8141 – 8155, 1997.
- [49] Liu. Y, Hagfeldt. A, Xiao. X, Lindquist, S. Sol. Energy Mater. Sol. Cells, vol.55, p.267 – 281, 1998.
- [50] Hara, K. et al. Sol. Energy Mater. Sol. Cells, vol.70, p.151 – 161, 2001.
- [51] Y. Liu, A. Hagfeldt, X. R. Xiao, and S. E. Lindquist, “ Investigation of influence of redox species on the interfacial energetics of a dye-sensitized nanoporous TiO₂ solar cell, ” Sol. Energ. Mat. Sol. Cells, vol.55, p.267, 1998.
- [52] 林明獻, “ 太陽電池技術入門 ” ,全華書局.
- [53] A. Kay, M. Gratzel, “ Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder, ” Sol. Energy Mater. Sol. Cells, vol.44, p.99 – 117, 1996.
- [54] 蘇青森, “ 真空技術 ” ,東華書局 [55] B.D Cullity and S.R. Stock, Elements of X-Ray Diffraction, 3rd Ed., Prentice-Hall Inc., p.167-171, 2001.
- [56] A. L. Patterson, “ The Scherrer Formula for X-Ray Particle Size Determination, ” Phys. Rev., 56, 978., 1939.
- [57] T. Kawashima, T. Ezurz, K. Okada, H. Matsui, K. Goto, N. Tanabe, “ FTO/ITO double-layered transparent conductive oxide for dye-sensitized solar cells, ” Journal of Photochemistry and Photobiology A: Chemistry, vol.164, p.199-202, 2004.