

氮化鎵之金屬歐姆接觸及其MOS光檢測器特性之研究

楊國輝、黃俊達

E-mail: 229500@mail.dyu.edu.tw

摘要

本論文的研究目標係以電漿濺鍍沉積的方式；製作出具有低電阻及高穿透率的Ti/GaN、ITO/Ti/GaN 歐姆接觸(ohmic contact)。

其次；我們使用低溫的液相沉積(liquid phase deposition；LPD)方法，將二氧化矽沉積於n型氮化鎵(n-type GaN)基材上，形成阻障層並製造出MOS的光檢測器，用以探討MOS的暗電流機制及其光學特性。

最後；利用兩階段快速退火的方式於純氧氣或空氣中，進行p型氮化鎵之鎂(Mg)原子活化，以提高其摻雜濃度和提高導電率。

本論文內容分為四大部份，分別敘述如下：

第一部份(第一章至第二章)：以電漿濺鍍沉積的方式，分別將鈦(Ti)及鈦/氧化銻錫(ITO)沉積於n型氮化鎵基材上形成良好的歐姆接觸，其特定接觸電阻(specific contact resistance)分別為 $8.7 \times 10^{-7} \text{ } \Omega\text{-cm}^2$ 和 $3.2 \times 10^{-6} \text{ } \Omega\text{-cm}^2$ 。在我們的研究裡，係採用射頻濺鍍系統將ITO沉積於n型氮化鎵基材上；形成良好的電流-電壓線性關係。這種方法有別於其他學者使用電子束蒸鍍沉積ITO，在他們的研究裡ITO與n-type GaN的接觸具有能障高度(barrier height)為0.68 eV，形成蕭特基接觸。

第二部份(第三章)：利用低成本的液相沉積方法，將二氧化矽有效地沉積於n型氮化鎵基材上，我們以超飽和六氟矽酸(H₂SiF₆)為沉積二氧化矽的源頭，硼酸(H₃BO₃)做為控制沉積速率的溶液並獲得最高的二氧化矽沉積速率為50.5 nm/hr。

第三部份(第四章)：以液相沉積法來製作MIS的阻障層並應用在Al-gate/20nm LPD-SiO₂/n-GaN和ITO-gate/LPD-SiO₂/n-GaN之MOS紫外線光檢測器。Al-gate MOS的界面電荷密度(Dit)於未退火前為 $8.4 \times 10^{11} \text{ cm}^{-2} \text{ V}^{-1}$ 。於真空中800 °C退火1小時後，其界面電荷密度降為 $1.75 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1}$ 。電場強度為(4 MV/cm)時，暗電流(dark current)密度為 $4.41 \times 10^{-6} \text{ A/cm}^2$ 。在照射波長為366nm的紫外線時，其響應度(responsivity)是0.112 A/W。對我們的ITO-gate MOS而言，其光-暗電流比可達到10⁴以上，其響應度(responsivity)為0.65 A/W。

第四部份(第五章)：使用兩階段快速退火(rapid thermal annealing；RTA)來活化p型氮化鎵薄膜的鎂雜原子濃度，並與使用一般爐管退火方式(conventional furnace annealing；CFA)來做比較。兩階段快速退火為，第一階段是在氧氣或空氣中，於750 °C下退火1分鐘。第二階段是在600 °C下退火5分鐘。我們發現採用兩階段快速退火方式，可獲得較高的電洞濃度及較低電阻的p型氮化鎵薄膜。

關鍵詞：氮化鎵、光檢測器、光電流

目錄

TABLE OF CONTENTS

SIGNATURE PAGE

LETTER OF AUTHORITY	iii
ENGLISH ABSTRACT	iv
CHINESE ABSTRACT	vi
ACKNOWLEDGMENTS	viii
TABLE OF CONTENTS	ix
LIST OF FIGURES	xi
LIST OF TABLES	xiv

Chapter 1 Nonalloyed Ti/indium tin oxide and Ti ohmic contacts to n-type GaN using plasma pre-treatment	1
1.1 Introduction	1
1.2 Experimental Techniques	2
1.3 Results and Discussions	3
Chapter 2 A novel transparent ohmic contacts of indium tin oxide to n-type GaN	11

2.1 Introduction	11
2.2 Experimental Techniques	12
2.3 Results and Discussions	12
Chapter 3 Extremely low temperature growth of silicon dioxide on gallium nitride by using liquid phase deposition	21
3.1 Introduction	21
3.2 Experimental Techniques	22
3.3 Results and Discussions	23
3.3.1 Dependence of thickness	
3.3.2 Leakage current density	24
3.3.3 Investigations of EDX, XPS and Auger depth-profile	25
Chapter 4 Nitride-Based UV Metal-Insulator-Semiconductor Photo-detector with Liquid-Phase-Deposition Oxide	38
4.1 Al-gate/SiO ₂ /n-GaN MIS photo-detectors	39
4.1.1 Introduction	40
4.1.2 Experimental Techniques	42
4.1.3 Results and discussion	42
4.2 ITO-gate/SiO ₂ /n-GaN MIS photo-detectors	43
4.2.1 Introduction	44
4.2.2 Experimental Techniques	45
4.2.3 Results and discussion	46
Chapter 5 Activation of Mg-doped P-GaN by using two-step annealing	58
5.1 Introduction	58
5.2 Experimental Techniques	59
5.3 Results and Discussions	60
Chapter 6 Conclusions	61
References	71
Bibliography	78

List of Figures

Fig. 1-1 RF sputtering system	6
Fig. 1-2 I-V characteristics of ITO/Ti/n-GaN and Ti/n-GaN samples	7
Fig. 1-3 Surface AES data for sample C and D	8
Fig. 1- 4 Transmittance of the ITO films in our studies	9
Fig. 1-5 A representative cross section of Ti and Ti/ITO ohmic contacts to n-type GaN	10
Fig. 2-1 I-V curves of ITO/n-GaN devices for sample A, B, and C	11
Fig. 2-2 Surface AES data for sample D and E	12
Fig. 2-3 Transmittance of sputtered ITO films with non-annealed and 500 °C annealed samples	13
Fig. 2-4 A representative ITO/n-type GaN cross section	14
Fig. 3-1 The preparation of the saturated solution of LPD-SiO ₂ and the deposition flowchart	21
Fig. 3-2 The thickness of LPD-SiO ₂ as a function of growth temperature for immersion time of 1 hour	

.	22
Fig. 3-3 The thickness of LPD-SiO ₂ versus deposition times for different concentrations of H ₂ SiF ₆ and H ₃ BO ₃	23
.	23
Fig. 3-4 The annealing effect, 800 °C in N ₂ ambient for 1 hour, on thickness of LPD-SiO ₂ films	24
.	24
Fig. 3-5 The leakage current density as a function of electric field for different concentrations of H ₃ BO ₃ (0.01 and 0.005M), but H ₂ SiF ₆ was kept at 0.5M	25
Fig. 3-6 The leakage current density as a function of electric field for different concentrations of H ₃ BO ₃ (0.01 and 0.005M), but H ₂ SiF ₆ was kept at 1M	26
Fig. 3-7 Annealing effect on leakage current density	27
Fig. 3-8 Element analysis of LPD-SiO ₂ by using EDX	28
Fig. 3-9 Composition analysis of LPD-SiO ₂ by using XPS	29
Fig. 3-10 Auger depth-profile for (a) as-grown and (b) annealed LPD-SiO ₂ films on GaN	30
.	30
Fig. 3-11 The Growth model of LPD-SiO ₂ on GaN	31
Fig. 4-1 Device structure of n-type GaN MIS photo-detector	47
Fig. 4-2 LPD-SiO ₂ thickness vs growth time under different growth temperatures for concentrations of H ₂ SiF ₆ (0.5 M) and H ₃ BO ₃ (0.01 M)	48
Fig. 4-3 AFM image of 20- nm- thick LPD-SiO ₂	49
Fig. 4-4 Film thickness versus growth time under different concentrations of H ₃ BO ₃ while H ₂ SiF ₆ in held constant at 0.5 M for nonannealed and annealed samples	50
Fig. 4-5 XPS spectrum of Si 2p core level for LPD-SiO ₂	51
Fig. 4-6 Dark I-V characteristic of Al/20nm LPD-SiO ₂ /n-GaN MIS capacitor	52
Fig. 4-7 Responsivity vs different reverse bias for MIS PD with 10-nm-thick LPD-SiO ₂ . The inset shows the current densities vs different applied bias for dark and photoilluminated PD	53
Fig. 4-8 Band diagram for defect-assisted tunneling. The holes tunnel through donorlike defects in LPD-SiO ₂ toward the Al gate electrode	54
Fig. 4-9 XPS spectrum of (a) Si2p and (b) O1s for LPD-SiO ₂ on GaN	55
Fig. 4-10 I-V characteristics of ITO/10-nm LPD-SiO ₂ /GaN MIS and ITO/GaN photodetectors measured in dark and under 366-nm illumination	56
Fig. 4-11 Spectral responsivity of GaN MIS UV photodetectors	57
Fig. 5-1 A representative cross section of Ni and Au ohmic contacts to p-type GaN	64
Fig. 5-2 I-V curves corresponding to different annealing cases	65
Fig. 5-3 Resistivity as a function of different annealing cases	66
Fig. 5-4 Concentration of different annealing cases	67
Fig. 5-5 SIMS profiles of hydrogen in as-deposited and case D sample	68
Fig. 5-6 PL spectrum for GaN samples annealed in a pure O ₂ ambient	69

List of Tables

Table 2-1 Different treatments of GaN samples and its specific contact resistance . 16

Table 5-1 Six sets of different experimental cases for activating Mg-doped p-type GaN film 63

參考文獻

- [1] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, *Jpn. J. Appl. Phys.* 34 (1995) L797.
- [2] S. Nakamura, T. Mokia, and M. Senoh, *Appl. Phys. Lett.* 64 (1994) 1689.
- [3] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyodo, *Appl. Phys. Lett.* 70 (1996) 868.
- [4] E. Kaninska, A. Piotrowska, M. Guziewicz, S. Kasjaniuk, A. Bracz, E. Dynowska, M. D. Bremser, O. H. Nam, and R. F. Davis, *Mater. Res. Soc. Symp. Proc.* 449 (1997) 1055.
- [5] J. D. Guo, C. I. Lin, M. S. Feng, F. M. Pan, G. C. Chi, and C. T. Lee, *Appl. Phys. Lett.* 68 (1996) 235.
- [6] M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoc, *Appl. Phys. Lett.* 64 (1994) 100.
- [7] Zhifang Fan, S. Noor Mohammad, Wook Kim, ?zg?r Aktas, Andrei E. Botchkarev, and Hadis Morkoc, *Appl. Phys. Lett.* 68 (1996) 1672.
- [8] J. K. Sheu, Y. K. Su, G. C. Chi, M. J. Jou, and C. M. Chang, *Appl. Phys. Lett.* 72 (1998) 3317.
- [9] J. K. Sheu, Y. K. Su, G. C. Chi, M. J. Jou, and C. M. Chang, *Solid-State Electronics* 43 (1999) 2081.
- [10] D. W. Jenkins and J. D. Dow, *Phys. Rev. B* 39 (1989) 3317.
- [11] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, *Jpn. J. Appl. Phys., Part 2* 34L (1995) 797.
- [12] S. J. Chang, W. C. Lai, Y. K. Su, J. F. Chen, C. H. Liu, and U. H. Liaw, *IEEE J. Sel. Top. Quan. Electron.*, 8 (2002) 278.
- [13] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyodo, *Appl. Phys. Lett.* 70(1996) 868.
- [14] J. S. Foresi and T. D. Moustakas, *Appl. Phys. Lett.* 62 (1993) 2859 .
- [15] J. D. Guo, C. I. Lin, M. S. Feng, F. M. Pan, G. C. Chi, and C. T. Lee, *Appl. Phys. Lett.* 68 (1996) 235.
- [16] M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoc, *Appl. Phys. Lett.* 64 (1994) 1003.
- [17] Z. Fan, S. N. Mohammad, W. Kim, ?. Aktas, A. E. Botchkarev, and H. Morkoc, *Appl. Phys. Lett.* 68 (1996) 1672.
- [18] Y. K. Su, S. J. Chang, C. H. Chen, J. F. Chen, G. C. Chi, J. K. Sheu, W. C. Lai, and J. M. Tsai, *IEEE Sensors Journal*, 2 (2002) 366.
- [19] J. K. Sheu, Y. K. Su, G. C. Chi, M. J. Jou, and C. M. Chang, *Solid-State Electronics* 43 (1999) 2081.
- [20] D. W. Kim, Y. J. Sung, J. W. Park, G. Y. Yeom, *Thin Solid Films*, 377 (2001) 398.
- [21] D. W. Jenkins and J. D. Dow, *Phys. Rev. B* 39 (1989) 3317.
- [22] S. J. Fonash, S. Ashok, and R. Singh, *Appl. Phys. Lett.* 39 (1981) 423.
- [23] M. J. Tsai, A. L. Fahrenbruch, and R. H. Bube, *J. appl. Phys.* 51 (1980) 2696.
- [24] S. Nakamura, M. Senoh, N. Iwasa and S. Nagahama: *Jpn. J. Appl. Phys.* 34 (1995) L797.
- [25] S. Nakamura, T. Mukai and M. Senoh: *Jpn. J. Appl. Phys.* 30 (1991) L1998.
- [26] S. J. Chang, W. C. Lai, Y. K. Su, J. F. Chen, C. H. Liu and U. H. Liaw: *IEEE J. Sel. Top. Quan. Electron.* 8 (2002) 278.
- [27] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kiyodo: *Appl. Phys. Lett.* 70 (1996) 868.
- [28] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto: *Jpn. J. Appl. Phys.* 35 (1996) L74.
- [29] C. K. Wang, R. W. Chuang, S. J. Chang, Y. K. Su, S. C. Wei, T. K. Lin, T. K. Ko, Y. Z. Chiou and J. J. Tang: *Mater. Sci. & Eng. B* 119 (2005) 25.
- [30] C. T. Lee, H. W. Chen and H. Y. Lee, *Appl. Phys. Lett.* 82 (2003) 4304.
- [31] T. Rotter, D. Mistele, J. Stemmer, F. Fiedler, J. Aderhold, J. Graul, V. Schwegler, C. Kirchner, and M. Kamp and M. Heuken: *Appl. Phys. Lett.* 76 (2000) 3923.

- [32] H. C. Casey, Jr., G. G. Fountain, R. G. Alley, B. P. Keller and Steven P. DenBaars: Appl. Phys. Lett. 68 (1996) 1850.
- [33] Kevin Matocha, Ronald J. Gutmann and T. Paul Chow: IEEE Trans. Electron Devices. 50 (2003) 1200.
- [34] S. J. Chang, Y. K. Su, F. S. Juang, C. T. Lin, C. D. Chiang and Y. T. Cherng: IEEE J. Quantum Electron. 36 (2000) 583.
- [35] C. T. Lin, Y. K. Su, S. J. Chang, H. T. Huang, S. M. Chang and T. P. Sun: IEEE Photo. Technol. Lett. 9 (1997) 232.
- [36] J. D. Hwang, G. H. Yang, W. T. Chang, C. C. Lin, R.W. Chuang and S.J. Chang: Microelectronic Engineering, 77 (2005) 71.
- [37] C. J. Huang, Jiann-Ruey Chen and S.P. Huang: Mater. Chem. & Phys. 70 (2001) 78.
- [38] J. S. Chou and S. C. Lee: Appl. Phys. Lett. 64 (1994) 1971.
- [39] M. P. Houg, C. J. Huang, Y. H. Wang, N. F. Wang and W. J. Chang: J. Appl. Phys. 82 (1997) 5788.
- [40] H. R. Wu, K. W. Lee, T. B. Nian, D. W. Chou, J. J. Huang, Y. H. Wang, M. P. Houg, P. W. Sze, Y. K. Su, S. J. Chang, C. H. Ho, C. I. Chiang, Y. T. Chern, F. S. Juang, T. C. Wen, W. I. Lee and J. I. Chyi: Mater. Chem. & Phys. 80 (2003) 329.
- [41] D. W. Chou, K. W. Lee, J. J. Huang, H. R. Wu, Y. H. Wang, M. P. Houg, S. J. Chang and Y. K. Su: Jpn. J. Appl. Phys. 41 (2002) L748.
- [42] K. W. Lee, D. W. Chou, H. R. Wu, J. J. Huang, Y. H. Wang, M. P. Houg, S. J. Chang and Y. K. Su: Electron. Lett. 38 (2002) 830.
- [43] J. D. Hwang, Z. Y. Lai, C. Y. Wu and S. J. Chang: Jpn. J. Appl. Phys. 44 (2005) 1726.
- [44] C. T. Lee, H. Y. Lee and H. W. Chen: IEEE Electron. Dev. Lett. 24 (2003) 54.
- [45] X. A. Cao, H. Cho, S. J. Pearton, G. T. Dang, A. P. Zhang, F. Ren, R. J. Shul, L. Zhang, R. Hickman, and J. M. Van Hove: Appl. Phys. Lett. 75 (1998) 232.
- [46] D. J. Fu, Y. H. Kwon, T. W. Kang, C. J. Park, K. H. Baek, H. Y. Cho, D. H. Shim, C. H. Lee and K. S. Chung: Appl. Phys. Lett. 80 (2002) 446.
- [47] J. I. Pankove: Mater. Res. Soc. Symp. Proc. 162 (1990) 515.
- [48] G. Parish, S. Keller, P. Kozodoy, J. A. Ibbetson, H. Marchand, P. T. Fini, S. B. Fleischer, S. P. DenBaars and U. K. Mishra: Appl. Phys. Lett. 75 (1999) 247.
- [49] Q. Chen, J. W. Yang, A. Osinsky, S. Gangopadhyay, B. Lim, M. Z. Anwar, M. Asif Khan, D. Kuksenkov and H. Temkin: Appl. Phys. Lett. 70 (1997) 2277.
- [50] P. Kung, X. Zhang, D. Walker, A. Saxler, J. Piotrowski, A. Rogalski and M. Razeghi: Appl. Phys. Lett. 67 (1995) 3792.
- [51] H. C. Casey, Jr., G. G. Fountain, R. G. Alley, B. P. Keller and S. P. DenBaars: Appl. Phys. Lett. 68 (1996) 1850.
- [52] K. Matocha, R. J. Gutmann and T. P. Chow: IEEE Trans. Electron Devices 50 (2003) 1200.
- [53] S. J. Chang, Y. K. Su, F. S. Juang, C. T. Lin, C. D. Chiang and Y. T. Cherng: IEEE J. Quantum Electron. 36 (2000) 583.
- [54] C. T. Lin, Y. K. Su, S. J. Chang, H. T. Huang, S. M. Chang and T. P. Sun: IEEE Photonics. Technol. Lett. 9 (1997) 232.
- [55] J. D. Hwang, G. H. Yang, W. T. Chang, C. C. Lin, R. W. Chuang and S. J. Chang: Microelectron. Eng. 77 (2005) 71.
- [56] C. J. Huang, J. R. Chen and S. P. Huang: Mater. Chem. Phys. 70 (2001) 78.
- [57] H. R. Wu, K. W. Lee, T. B. Nian, D. W. Chou, J. J. Huang, Y. H. Wang, M. P. Houg, P. W. Sze, Y. K. Su, S. J. Chang, C. H. Ho, C. I. Chiang, Y. T. Chern, F. S. Juang, T. C. Wen, W. I. Lee and J. I. Chyi: Mater. Chem. Phys. 80 (2003) 329.
- [58] D. W. Chou, K. W. Lee, J. J. Huang, H. R. Wu, Y. H. Wang, M. P. Houg, S. J. Chang and Y. K. Su: Jn. J. Appl. Phys. 41 (2002) L748.
- [59] M. L. Lee, J. K. Sheu, W. C. Lai, S. J. Chang, Y. K. Su, M. G. Chen, C. J. Kao, G. C. Chi and J. M. Tsai: Appl. Phys. Lett. 28 (2003) 2913.
- [60] B. C. Hsu, S. T. Chang, T. C. Chen, P. S. Kuo, P. S. Chen, Z. Pei and C. W. Liu: IEEE Electron Device. Lett. 24 (2003) 318.
- [61] Y. Z. Chiou, Y. K. Su, S. J. Chang, J. Gong, C. S. Chang, and S. H. Liu: J. Electron. Mater. 32 (2003) 395.
- [62] J. D. Hwang, and C. C. Lin: Thin Silid Films, 491 (2005) 276.
- [63] J. I. Pankove: Mater. Res. Soc. Symp. Proc. 162 (1990) 515.
- [64] S. Arulkumaran, T. Egawa, H. Ishikawa, T. Jimbo, and M. Umeno: Appl. Phys. Lett. 73 (1998) 809.
- [65] D. Fu, and T. W. Kang: Jpn. J. Appl. Phys. 41 (2002) L1437.
- [66] C. T. Lee, H. Y. Lee, and H. W. Chen: IEEE Electron Device Lett. 24 (2003) 54.
- [67] J. S. Chou and S. C. Lee, Appl. Phys. Lett. 64 (1994) 1971.
- [68] C. J. Huang, M. P. Houg, Y. H. Wang, H. H. Wang, J. Appl. Phys. 86 (1999) 7151.
- [69] J. D. Hwang, Gwo Huei Yang, Yuan Yi Yang and Pin Cuan Yao: Jpn. J. Appl. Phys. 44 (2005) 7913.
- [70] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Jpn. J. Appl. Phys. Part 2 Letter 34 (1995) L797-800 .
- [71] S. Nakamura, T. Mokia, and M. Senoh, Appl. Phys. Lett. 64 (1994) 1689.
- [72] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyodo, Appl. Phys. Lett. 70 (1996) 868.
- [73] D. W. Jenkins and J. D. Dow, Phys. Rev. B 39 (1989) 3317.
- [74] J. I. Pankove: Mater. Res. Soc. Symp. Proc. (1990) 160:515.
- [75] S. W. Kim, J. M. Lee, Chul Huh, N. M. Park, H. S. Kim, I. H. Lee, and S. J. Park, Appl. Phys. Lett. 70 (2000) 3079.
- [76] S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, Jpn. J. Appl. Phys. Part 2 Letter 31 (1992) L139-2.
- [77] C. H. Kuo, S. J. Chang, Y. K. Su, L. W. Wu, J. K. Sheu, C. H. Chen and G. C. Chi, Jpn. J. Appl. Phys. Part 2 Letter 41 (2002) L112-5.
- [78] H.C. Cheng, C.Y. Huang, F.S. Wang, K.H. Lin, F.G. Tarntair; Jpn. J. Appl. Phys. Part 2 Letter 39 (2000) L19-21.

[79] James D. Plummer, Michal D. Deal, Peter B. Griffin, Silicion VLSI technology, Prentice Hall, Inc. U.S.A.