

Exploration of the hafnium oxide films grown by thermal oxidation

楊尚剛、NOTE

E-mail: 344704@mail.dyu.edu.tw

ABSTRACT

In this thesis, hafnium was using thermal oxidation to the preparation of metal oxide for the rare earth element hafnium metal. Hafnium metal was deposited on silicon wafer by E-Gun and then proceeded with thermal oxidation in high temperature furnace tube for various oxidation temperature (600 ~ 900). The Capacitance-voltage (C-V) characteristic curve was measured by LCR Meter (1 MHz) high-frequency range and calculated for each sample of the oxide dielectric constant () are greater than 25. By the instrument HP4156C measurements when the bias is -1V, the samples leakage current density are less than 10⁻⁷ A/cm² and the breakdown field strength are more than 9 MV/cm. The greater thickness of oxide film was obtained for the longer oxidation temperature by the transmission electron microscopy (TEM) measurement. The surface morphology of hafnium oxide films was measured by atomic force microscope (AFM). From the macro point of view, the grown oxide films of which thickness, surface roughness (Ra) vary with oxidation temperature. The crystal structure, showing tetrahedral shape into six-sided cone (Hexahedron) extent that octahedral pyramid (Octahedron), the nuclei of hafnium oxide started growing from the bottom (substrate surface) and gradually stacking up into a taper, there are similarities between the present pattern after rolling through the taper tip, the measure on surface of the oxidation films by Nanoscope III.

目錄 封面內頁 簽名頁 中文摘要	iii Abstract	iv 誌謝
v 目錄	viii 表目錄	vi 圖目錄
1.1研究背景	1 1.2研究方法	2 2.1高介電薄膜介紹
1.3論文結構	3 第二章 文獻回顧	2.2 HfO ₂ 薄膜特性
4	2.1.1材料的選擇	2.3 MOS製程特性與基礎
6	5	7
8 電晶體(NMOS)	2.3.2 P-channel金氧半場效電晶體(PMOS)	10 2.3.1 N-channel金氧半場效
11	11 2.4氧化層薄膜物理特性	11 2.3.3 臨界電壓
13 1.研究背景	13 3.1前言	xi 第一章 緒論
15 1.2研究方法	14 3.2.1二氧化矽(SiO ₂)薄膜製備	2 2.1高介電薄膜介紹
18 1.3論文結構	16 3.2.2二氧化矽(SiO ₂)薄膜電氣特性	2.2 HfO ₂ 薄膜特性
20 2.1.1材料的選擇	18 3.3厚度30A與100 A的鎔金屬氧化物薄膜製備	2.3 MOS製程特性與基礎
31 量測與分析	22 4.3氧化鎔薄膜表面粗糙度(Surface Roughness)的量測	2.3.1 N-channel金氧半場效電晶體(NMOS)
38 4.3氧化鎔薄膜表面粗糙度(Surface Roughness)的量測	43 4.6氧化鎔的電容—電壓特性	8 2.3.2 P-channel金氧半場效電晶體(PMOS)
44 5.2未來研究方向	46 5.2未來研究方向	11 2.4氧化層薄膜物理特性
46 參考文獻	48 參考文獻	

Keywords : hafnium oxide、transmission electron microscopy (TEM)、atomic force microscope (AFM)、surface roughness (Ra)

Table of Contents

目錄 封面內頁 簽名頁 中文摘要	iii Abstract
iv 誌謝	v 目錄
vi 圖目錄	viii 表目錄
xi 第一章 緒論	1.1研究背景
1 1.2研究方法	2 1.3論文結構
3 第二章 文獻回顧	2.1高介電薄膜介紹
5 與基礎	4 2.1.1材料的選擇
7 金氧半場效電晶體(PMOS)	6 2.2 HfO ₂ 薄膜特性
10 理特性	8 2.3 MOS製程特性與基礎
11 第三章 热氧化法應用於氧化鎔薄膜之研究	10 2.3.1 N-channel金氧半場效電晶體(NMOS)
	11 2.3.2 P-channel金氧半場效電晶體(PMOS)
	11 2.4氧化層薄膜物理特性
	3.1前言

裝備	13	3.2 實驗規劃	13	3.2.1 二氧化矽(SiO ₂)薄膜
氧化物薄膜裝備	14	3.2.2 二氧化矽(SiO ₂)薄膜電氣特性	15	3.3 厚度30A與100 A的鎵金屬
第四章 結果與討論 4.1 X-Ray繞射儀(XRD)對氧化鎵晶體結構的探討	18	20	4.2 穿透式電子顯微鏡(TEM)對氧化鎵結構橫剖面的探討	20
氧化物薄膜製備	16	4.4 X-Ray光電子頻譜儀(XPS)量測與分析	31	4.3 氧化鎵薄膜表面粗糙度(Surface Roughness)的量測
式電子顯微鏡(TEM)對氧化鎵結構橫剖面的探討	22	38	4.5 氧化鎵薄膜束縛能能階(Binding Energy)之分析與探討	38
4.7 氧化鎵的電流—電壓特性	44	46	4.6 氧化鎵的電容—電壓特性	46
論	43	第五章 結論與未來方向	46	5.1 結論
文獻	48			46 參考文獻

REFERENCES

- [1] P. Singer, " New Gate Dielectric Material Needed, " Semiconductor International , 38, 1998.
- [2] J. H. Stathis, A. Vayshenker, P. R. Varekamp, E. Y. Wu, C. Montrose, J. McKenna, D. J. DiMaria, L. – K. Han, E. Cartier, R. A. Wachnik and B. P. Linder, " Breakdown measurements of ultra-thin SiO₂ at low voltage, " IEDM Tech. Dig., 94,2000.
- [3] Kwo, J., Hong, M., Kortan, A. R., and Queeney, K. L., " Properties of High-k Gate Dielectrics Gd₂O₃ and Y₂O₃ for Si, " J. Appl.Phys., Vol. 89,pp. 3920-3927,2001.
- [4] Kim, Joong-Do., Pyun, Su-II., and Seo, Masahiro., " Effect of Hydrogen on Stresses in Anodic Oxide Film on Titanium, " Electrochimica Acta, 48, pp. 1123-1130, 2003.
- [5] Yanagisawa, Hideto., Kamijyo, Masahiro., Shinkai, Satoko., Sasaki, Katsutaka., ABE, Yoshio., and Yamane, Misao., " Electrical Properties of HfO₂ Thin Insulating Film Prepared by Anodic Oxidation, " J. J. Appl. Phys. Vol. 41, pp. 5284-5287, 2002.
- [6] Lee, S. J., Choi, C. H., Kamath, A., Clark R., and Kwong, D. L., " Characterization and Reliability of Dual High-k Gate Dielectric Stack (Poly-Si- HfO₂- SiO₂) Prepared by in Situ RTCVD Process for System-on-Chip Applications, IEEE Electron Device Letters, Vol. 24, No.2, February 2003.
- [7] Lee, Byoung Hun., Kang, Laegu., Nieh, Renee., Qi, Wen-jie., and Lee, Jack C., " Thermal Stability and Electrical Characteristics of Ultrathin Hafnium Oxide Gate Dielectric Deoxidized with Rapid Thermal Annealing, " Appl. Phys. Lett., Vol. 76, No. 14, 3, April, 2000.
- [8] Kang, Laegu., Lee, Byoung Hun., Qi, Wen-Jie., Jeon, Yongjoo., Nieh, Renee., Gopalan, Sundar., Onishi, Katsunori., and Lee, Jack C., " Electrical Characteristics of Highly Reliable Ultrathin Hafnium Oxide Gate Dielectric, " IEEE Electron Device Letters, Vol. 21, No.4, April 2000.
- [9] Callegari, A., Cartier, E., Gribelyuk, M., Okorn-Schmidt, H. F., and Zabel, T., " Physical and Electrical Characterization of Hafnium Oxide and Hafnium Silicate Sputtered Films, " J. Appl. Phys., Vol. 90, No. 12, 15, December 2001.
- [10] Gusev, E. P., Cartier, E., Buchanan, D. A., Gribelyuk, M., Copel, M., Okorn-Schmidt, H., and Emic, C. D., " Ultrathin High-K Metal Oxides on Silicon: Processing Characterization and Integration Issues, " Microelectronic Engineering, 59, pp. 41-319, 2001.
- [11] Xiong, Yueping., Yamaji, Katsuhiko., Sakai, Natsuko., Negishi, Hideyuki., Horita, Teruhisa., and Yokokawa, Harumi., " Electronic Conductivity of ZrO₂—CeO₂—YO 1.5 Solid Solutions, " J. Electrochem. Soc., 148, (12), pp. E489-E492, 2001 .
- [12] Koh, B. H, Ng, T. H., Zheng, J. X., Chim, W. K., and Choi, W. K., " Quantum Mechanical Modeling of Capacitance and Gate Current for MIS Structures Using Zirconium Dioxide as the Gate Dielectric, " ICSE ' 02 Proc., Penang Malaysia, pp. 135-140, Dec. 2002.
- [13] Lim, Kwan-Yong., Park, Dae-Gyu., Cho, Heung-Jae., Kim, Joong-Jung., Yang, Jun-Mo., Choi, II-Sang., Yeo, In-Seok., and Park, Jin Won., " Electrical Characteristics and Thermal Stability of n+Polycrystalline-Si/ZrO₂/SiO₂/Si MetalOxideSemiconductor Capacitors, " J. Appl. Phys., Vol. 91, No.1, 1 January 2002.
- [14] EL-Mahdy, G. A., Mahmoud, S. S., and El-Dahan, H. A., " Effect of Halide Ions on the Formation and Dissolution Behaviors of Zirconium Oxide, " Thin Solid Films, 286, pp. 289-294, 1996.
- [15] Lue, Hang-Ting., Liu, Chih- Yi., and Tseng, Tseung-Yuen., " An Improved Two-Frequency Method of Capacitance Measurement for SrTiO₃ as High-k Gate Dielectric, " IEEE Electron Device Letters, Vol. 23, No.9, September 2002.
- [16] Tzeng, Pei-Jer., Chang, Yi-Yuan., and Chang-Liao, Kuei-Shu., " Plasma Charging Damage on MOS Devices with Gate insulator of High-Dielectric Constant Material, " IEEE, Electron Device Letters, Vol. 22, No. 11, November 2001.
- [17] Roussel, Philippe., Degraeve, Robin., Kerber, Andreas., Pantisano, Luigi., and Groeseneken, Guido., " Accurate Reliability Evaluation of Non-Uniform Ultrathin Oxynitride and High-k Layers, " IEEE 03CH37400, 41 st Annual International Reliability Physics Symposium, Dallas, Texas, pp. 29-33, 2003.
- [18] Xu, Jianwen., and Wong, C. P., " Effects of the Low Loss Polymers on the Dielectric Behavior of Novel Aluminum-Filled High-K Nano-Composites, " IEEE 9th Int ' l Symposium on Advanced Packaging Materials, pp. 158-170, 2004.
- [19] Laversenne, L., Guyot, Y., Goutaudier, C., Cohen-Adad, M. Th., and Boulon, G., " Optimization of Spectroscopic Properties of Yb³⁺-Doped Refractory Sesquioxides: Cubic Y₂O₃, Lu₂O₃ and Monoclinic Gd₂O₃, " Optical Materials 16, pp. 475-483, 2001.
- [20] Chen, J. C., Shen, G. H., and Chen, L. J., " Interfacial Reactions of Gd Thin Films on (111) and (001) Si, " Appl. Surf. Sci., 142, pp.

- [21]Hussein, G. A. M., Khedr, M. H., and Farghali, A. A., "Gadolinium Oxide from Gadolinium Oxalate Hydrate Physicochemical Characterization," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 203, pp. 137-142,2002.
- [22]Ko, Hong-Hsi., Chang, Liann-Be., Jeng, Ming-Jer., Kuei, Ping-Yu., and Horng, Kuo-Yang., "Properties of Thermal gadolinium Oxide Films on Silicon," *J. J. Appl. Phys.*, Vo1. 44, No. 5A, pp. 3205-3208,2005.
- [23]Hsieh, Li-Zen., Ko, Hong-Hsi., Kuei, Ping-Yu., Chang, Liann-Be., and Jeng, Ming-Jer., "Hysteresis in Gadolinium Oxide Metal-Oxide-Semiconductor Capacitors," *J. Appl. Phys.*, Vol. 98, No.7, 1 October 2005.
- [24]T. Wang, C. T. Chan and C. J. Tang et al., "Novel Transient Characterization Technique to Investigate Trap Properties in HfSiON Gate Dielectric MOSFETs," From Single Electron Emission Devices. (ITED), 53,pp.1073-1079 ,2006.
- [25]陳怡誠，交通大學電子研究所碩士，高介電薄膜簡介。
- [26]譚立威，反應濺鍍氧化鉭與氧化鈴薄膜特性之研究，2004。
- [27]孫允武，半導體物理與元件5-1場效電晶體原理，中興物理。
- [28]孫允武，應用電子學7-4 MOS的操作原理，中興物理。
- [29]Hong Xiao,譯者:羅正忠，半導體製程技術導論(修訂版)，學銘圖書股份有限公司，歐亞書局有限公司，2006。
- [30]Chen,J. C., Shen G.H., and Chen, L. J., "Formation of Gd Oxide Thin Films on (111) Si," *Appl. Surf. Sci.*, Vol. 142, pp.120-123, 1999.
- [31]Grecea, M., Rtaru, C.,Nastase, N., and Cracium, G., "Physical Properties of SiO₂ Thin Films Obtained by Anodic Oxidation," *J. Molecular Structure*,480-481,pp. 607-610, 1999.
- [32]Lee, C. H., Yeh, C. C., and Hsu, K. Y. J., "Formation of Bottom Oxides in Porous Silicon Films by Anodic Oxidation," *Appl. Surf. Sci.*, Vol. 92, pp. 621-625, 1996.
- [33]Guerrero-Lemus, R., Ben-Hander, F. A., Martin-Palma R. J., Martinez-Duart, J. M., Gomez-Garrido, P., Marcos, M.L., and Gonzalez-Velasco, J., "Anodic Oxidation of Porous Silicon Bilayers," *J. Luminescence*, Vol. 80,pp. 173-178,1999.
- [34]Rappich, J., "Smoothing, Passivation and Re-Passivation of Silicon Surfaces by Anodic Oxidation: A Low Thermal Budget Process," *Microelectronics Reliability*, Vol. 40, pp.815-819,2000.
- [35]Bonoli, F., Godio, P., Borionetti, G., and Falster, R., "Gate Oxide Integrity Dependence on Substrate Characteristics and SiO₂ Thickness," *Materials Science in Semiconductor Processing*, Vol. 4, pp. 145-148, 2001.
- [36]DUMIN,DAVID J., "Characterizing Weaout, Breakdown and Trap Generation in Thin Silicon Oxide," *Microelectron Reliab.*, Vol. 37, No.7, pp. 1029-1038,1997 [37]Tsuzuki, T., Pirault, E., and McCimick, P. G., "MECHANOCHEMICAL SYNTHESIS OF GADOLINIUM OXIDE NANOPARTICLES," *Nano Structured Materials*, Vol. 11, No. 1,pp. 125-131, 1999.
- [38]Yacoby, Y., Sowwan, M., Stern, E., Cross, J., Brewe, D., Pindak, R., Pitney, J., Dufresne, Eric M., and Clarke, R., "Direct Determination of epitaxial interface Structure in Gd₂O₃ Passivation of GaAs," *Nature Materials*, Vol.1,pp.99-101.October 2002 [39]Yakovkin, I. N., Waldorfried, C., Komesu, TakaShi., and Dowben, P. A., "Variations of the Wave Vector Dependent Band Gaps wish Structural Transformations of Gd Thin Films," *Physics Letters A*,304,pp.43-48,2002.