Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) S475–S479

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Comparison of oxidized/nitrided Zr thin films on Si and SiC substrates

Yew Hoong Wong, Kuan Yew Cheong*

Energy Efficient & Sustainable Semiconductor Research Group, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal 14300, Penang, Malaysia

Abstract

This work utilizes simultaneous thermal oxidation and nitridation technique to transform sputtered Zr to ZrO_2 and to Zr-oxynitride thin films on Si and SiC substrates, respectively, in nitrous oxide gas ambient. Various characterization techniques such as X-ray photoelectron spectroscopy, energy-filtered transmission electron spectroscopy, atomic force microscopy, X-ray diffraction, capacitance–voltage measurements, and leakage current density-electric field measurements were carried out to evaluate and compare the structural, chemical, and electrical properties of the films produced on both Si and SiC substrates.

Keywords: Thin film; Oxide; D. Nitride

1. Introduction

In Si-based metal-oxide-semiconductor (MOS) devices, when the thickness of SiO_2 is less than 1.2 nm, the occurrence of relatively huge leakage current through the oxide, due to direct tunneling of carriers, is highly possible [1,2]. To proportionally shrink the dimension of a MOS structure without affecting the electrical designs [1,2], it is convenient to define an equivalent oxide thickness (*EOT*) as the thickness of high dielectric constant (κ) material that would be required to have the same capacitance as SiO_2 [1,2]. Hence, by developing high-κ oxides on Si, this will allow scaling to a thinner *EOT*. On the other hand, in SiC-based MOS devices, since the κ value of SiO_2 (3.9) is lower than SiC (10), it limits the permissible electric field in SiC-based devices [3]. As a result, the gate oxide may electrically break down prior to the SiC substrate thus making the usage of SiC as the substrate for high-power and high-temperature applications meaningless. In short, the integration of high-κ oxides on Si is to solve the down-scaling issues, while integration of high-κ oxides on SiC is to lower the electric field being imposed on the gate oxide itself.

Of several high-κ gate oxides, ZrO_2 has attracted much attention owing to its high κ value (22–25), large energy bandgap (5.8–7.8 eV), and it is easily stabilized in the form of cubic or tetragonal polymorphs, which may further enhance its effective κ value [1,2]. In addition, it also possesses good thermodynamic stability when in contact with Si and it has minimal lattice mismatch with Si (1 0 0) [4].

The quality of ZrO_2 thin film is very much dependent on the deposition technique. According to literatures, stoichiometric ZrO_2 thin films were successfully formed by a combination of Zr sputtering with thermal oxidation in O_2 ambient [5–9]. However, an undesirable interfacial layer (IL) has formed along with the formation of ZrO_2. Consequently, capacitance of the MOS structure is reduced. According to literatures [10–12], incorporation of nitrogen into the film could retard the growth of IL and improved electrical properties of the film.

To perform oxidation and nitridation simultaneously, NO and N_2O are the typical gases used [12]. Since N_2O is less toxic as compared to NO [13], hence, N_2O is preferable to be used. In this work, simultaneous thermal oxidation and nitridation technique was used to transform sputtered Zr to ZrO_2 and to Zr-oxynitride on Si and SiC, respectively, in N_2O gas ambient. The optimized oxidation/nitridation temperature and time were tabulated in Table 1. For Si-based samples, the oxidation/nitridation temperature was optimized at 700 °C,

---

*Corresponding author. Tel.: +60 45995259; fax: +6045941011.
E-mail address: cheong@eng.usm.my (K.Y. Cheong).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.117

whereas for SiC-based samples, the temperature was optimized at 500 °C, for 15 min in both samples. In this paper, structural, chemical, and electrical properties of oxidized/nitrided Zr on Si and SiC are compared.

2. Experimental procedures

Si [n-type, (1 0 0)-oriented, 1–10 Ωcm] and 4H-SiC [n-type, (0 0 0 1)-oriented, Si-faced, 0.020 Ωcm] were used as the starting substrates. Both substrates were cleaned by a standard RCA cleaning method and treated with a diluted HF solution (1 HF: 50 H_2O) for 15 s to remove native oxide from the surface prior to Zr sputtering. Edwards Auto 500 RF sputtering system was used to deposit an ultrathin 5-nm Zr film on the cleaned Si and SiC substrates by using a Zr target (Alfa Aesar, 99.5%). RF power, working pressure, and inert Ar gas flow were regulated at 170 W, 1.2×10^{-7} Torr, and 20 cm^3/min, respectively. Si- and SiC-based samples were placed into a horizontal tube furnace and heated up from room temperature to 500 °C and 700 °C, respectively, in an Ar flow ambient and the heating rate was set constant at 10 °C/min. Once the set temperature was achieved, N_2O gas was then introduced with a flow rate of 150 mL/min for 15 min. Samples were then taken out at room temperature after the furnace was cooled down to room temperature in an Ar ambient.

Properties of the films on Si and SiC were evaluated by various characterizations, as described elsewhere [14–17]. Compositions and depth profile of the films were conducted by Kratos Axis UltraDLD X-ray photoelectron spectroscopy (XPS), cross-sectional images of the films were analyzed by Zeiss Libra 200 energy filtered transmission electron microscopy (EFTEM), crystallinity of the films were characterized by P8 Advan–Bruker X-ray diffraction (XRD) system, the surface topography and root-mean-square (RMS) roughness of the samples were analyzed by Nano Navi SPI3800N atomic force microscope (AFM) using a noncontact mode, with 3×3 μm^2 scanned surface areas.

MOS capacitors were fabricated for electrical characterization. 100-nm thick Al was evaporated on top of the films. An array of 9×10^{-4} cm^2 of Al electrode was then photolithographically patterned using a shadow mask. Lastly, a back contact was fabricated by depositing a 100-nm thick Al film on backside of the Si and SiC after removal of native oxide. The electrical properties of the MOS capacitors were then characterized by high-frequency (1 MHz) capacitance–voltage (*C–V*) and current–voltage (*I–V*) measurements using Agilent HP4284 LCR meter and HP4155-6C semiconductor parameter analyzer (SPA), respectively.

Table 1
Optimized parameters of simultaneous oxidation and nitridation of sputtered Zr on different semiconductor substrates of Si and SiC in 100% N_2O.

Base substrate	Optimized temperature (°C)	Optimized duration (min)
Si	700	15
SiC	500	15

3. Results and discussion

3.1 Structural and chemical properties

Structural and chemical properties of oxidized/nitrided Zr thin films on Si and SiC substrates in 100% N_2O are compared in Table 2. It shows that ZrO_2 was formed with IL of Zr-silicate oxynitride (ZrSiON) on Si-based substrate, while Zr-oxynitride (ZrON) was formed with an IL comprised of ZrSiON and carbon nitride (CN) on SiC-based substrate. In both Si-based and SiC-based samples, IL of ZrSiON was produced with different combinations of mixed compounds. Distribution of nitrogen in the SiC-based sample is more uniform, with higher maximum atomic percent, as compared to Si-based sample. However, the conduction band offsets (ΔE_c) of SiC-based sample is lower than Si-based sample, owing to the combination of relatively narrower bandgaps of

Table 2
Comparison of structural and chemical properties of oxidized/nitrided sputtered Zr based on Si and SiC substrates.

Charac-terization tools	Properties	Unit	Si-based	SiC-based
XPS	Chemical composition of bulk	–	ZrO_2 (Zr–O) [14]	Zr-oxynitride (Zr–O and Zr–O–N) [17]
	Chemical composition of IL	–	Zr–O, Zr–N, Zr–Si–O, and Si–N [14]	Zr–O, Zr–N, Zr–O–N, Si–N, and C–N [17]
	Distribution profile of nitrogen	–	Relatively less uniform	Relatively more uniform
	Maximum atomic percent of nitrogen	at%	2.20 [14]	2.71
	E_g of bulk extracted from XPS	eV	6.40 [16]	5.00
	E_g of IL extracted from XPS	eV	8.80 [16]	8.50
	ΔE_c extracted from XPS	eV	3.40 [16]	2.00
EFTEM	Thickness of bulk	nm	6.00 [14]	16.90 [17]
	Thickness of IL	nm	4.00 [14]	1.86 [17]
	Total thickness (Bulk+IL)	nm	10.00 [14]	18.76 [17]
AFM	RMS value	nm	0.50	2.45 [17]
XRD	t-ZrO_2 planes	–	(1 0 1) and (0 0 2) [14]	(0 1 1) and (0 0 2) [17]

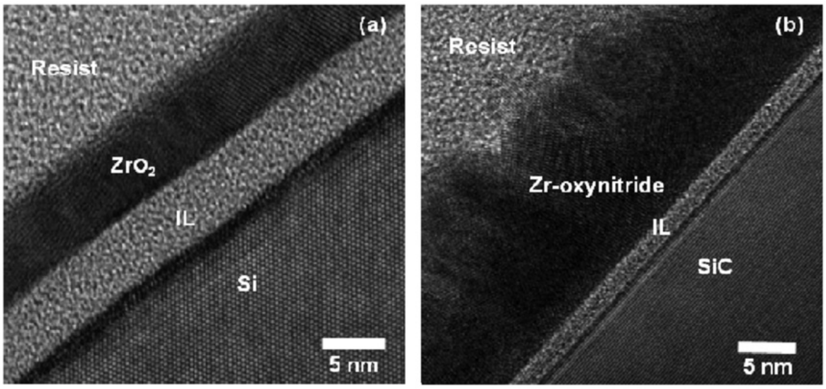

Fig. 1. Cross-sectional EFTEM images of (a) ZrO_2 on Si substrate [14] and (b) Zr-oxynitride on SiC substrate [17].

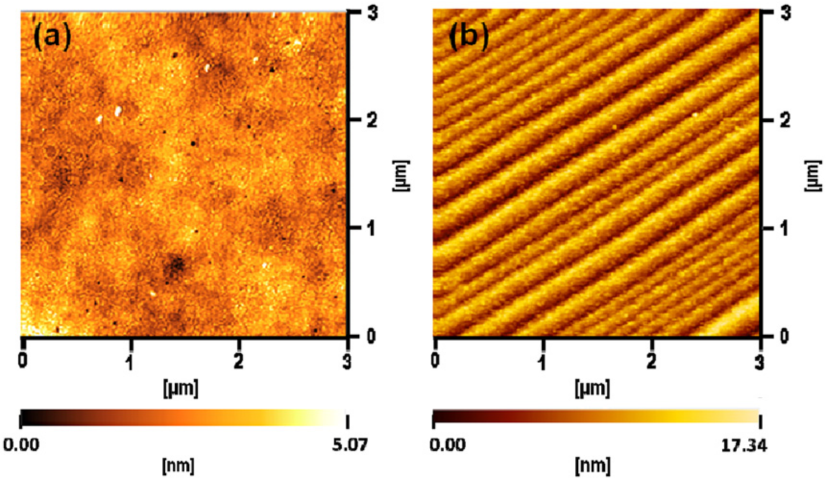

Fig. 2. Two-dimensional AFM surface topography of (a) ZrO_2 on Si substrate and (b) Zr-oxynitride on SiC substrate [17].

Zr-oxynitride and IL. This could lead to a reduced breakdown field of the sample. Through EFTEM analysis (Fig. 1 and Table 2), a thicker Zr-oxynitride, with a thinner IL was produced on SiC-based substrate as compared to Si-based substrate. This could help in enhancing the oxide capacitance (C_{ox}) and κ value of the film on SiC-based sample. There are two different two-dimensional (2D) surface topographies of ZrO_2 and Zr-oxynitride on Si and SiC substrates, respectively, as shown in Fig. 2. The produced Zr-oxynitride is in wavy topography on SiC substrate, while ZrO_2 is in non-wavy topography. With that, it was found that the ZrO_2 thin film on Si substrate has smoother surface, with lower RMS value, as compared to Zr-oxynitride thin film on SiC substrate. The crystalline planes of t-ZrO_2 on Si-based sample are (1 0 1) and (0 0 2), whereas on SiC-based sample are (0 1 1) and (0 0 2).

3.2 Electrical properties

Table 3 compares the electrical properties of oxidized/nitrided Zr thin films on Si and SiC in 100% N_2O, in terms of C–V and leakage current density–electric field (J–E) characteristics. It shows that SiC-based sample has higher C_{ox} than Si-based sample. This is attributed to the higher κ value and/or reduced IL thickness. As possessed in the table, the κ value of the film in SiC-based sample is double the κ value of the film in Si-based sample, whilst the IL thickness in the SiC-based sample is halve the IL thickness in the Si-based sample. SiC-based sample showed an enormous C–V curve shift to the positive voltage. This has been affirmed by the presence of enormous amount of negative effective oxide charge (Q_{eff}) in the oxide. As for Si-based sample, the C–V is shifted slightly to the negative voltage, thus, a lower positive Q_{eff} was recorded. A relatively larger hysteresis, with higher STD of one order of magnitude, was identified as compared in SiC-based sample to Si-based sample. Interface-trap density (D_{it}) and total interface-trap density (D_{total}) in SiC-based sample is higher than in Si-based sample. According to J–E characteristics, SiC-based sample has lower breakdown field (E_{HDB}) than Si-based sample. This could be due to higher Q_{eff}, STD, D_{it}, D_{total}, and lower ΔE_c (Table 2) in the SiC-based sample. The barrier height between the oxide and the semiconductor (ϕ_B) obtained in SiC-based sample is higher than in Si-based sample. The difference in ΔE_c and ϕ_B may be ascribed to the following reasons and assumptions [18]. Firstly, by using Fowler–Nordheim (FN) plot, the calculated ϕ_B takes into account of barrier height

Table 3
Comparison of electrical properties of oxidized/nitrided sputtered Zr based on Si and SiC substrates.

Measure-ments	Properties	Unit	Si-based	SiC-based
C–V	C_{ox}	pF	1731 [15]	2147 [17]
	Q_{eff}	cm^{-2}	$+4.50\times10^{11}$ [15]	-5.00×10^{13} [17]
	STD	cm^{-2}	4.62×10^{11} [15]	$+6.00\times10^{12}$ [17]
	D_{it} at $(E_c-E)=0.15$–0.25 eV	$eV^{-1}\,cm^{-2}$	Mid 10^{12}–10^{13} [15]	10^{14} [17]
	D_{total}	cm^{-2}	7.00×10^{12} [15]	3.70×10^{13} [17]
	κ	–	21.82 [15]	49.68 [17]
	E_{HDB}	MV/cm	13.60 [15]	5.05 [17]
J–E	J	A cm^{-2}	10^{-6} [15]	10^{-6} [17]
	ϕ_B	eV	1.33 [15]	1.67 [17]

lowering and quantization of electrons at the semiconductor surface and it is not strictly constant. Secondly, it could be attributed to the electron and oxide effective masses.

4. Conclusion

100% N_2O was used as the oxidation and nitridation source to form ZrO_2 thin film with an IL of ZrSiON on Si and to form oxynitrided Zr (ZrON) thin film with an IL comprises ZrSiON and CN on SiC. Formation of these compounds is due to dissociation of the N_2O gas into oxygen and nitrogen source that are used for oxidation and nitridation processes; in which the oxidation and nitridation rates may determine the final products. Though the studies provided high enough effective dielectric constant values (ZrO_2/IL/Si: 10.58–21.82; ZrON/IL/SiC: 42.32–50.20), however, the recorded densities of effective oxide charge, slow-trap, and interface-trap were still considerably high. It is hypothesized that dilution of N_2O may be a possible way to adequately produce a better quality oxide according to the accumulated knowledge [13,19–23] from thermally nitrided and oxidized Si on SiC to form nitrided SiO_2 gate. During this process, nitrogen source may enhance removal of carbon that has been accumulated at the interface during thermal oxidation and may improve passivation of dangling bonds on surface of the semiconductor depending on the equilibrium rate of oxidation and nitridation that has been achieved by diluting the oxidation and nitrogen sources [13], i.e., N_2O gas.

Acknowledgements

This project is supported by The Academy of Sciences for the Developing World through TWAS-COMSTECH Research Grant and partly supported by Long Term Research Grant, Ministry of Higher Education Malaysia (2011–2016) with Universiti Teknologi Petronas (Noorhana Yahya) under the OneBaja Project.

References

[1] J. Robertson, High dielectric constant oxides, European Physical Journal Applied Physics 28 (2004) 265–291.

[2] G.D. Wilk, R.M. Wallace, J.M. Anthony, High-κ gate dielectrics: current status and materials properties considerations, Journal of Applied Physics 89 (2001) 5243–5275.

[3] L.A. Lipkin, J.W. Palmour, Insulator investigation on SiC for improved reliability, IEEE Transactions on Electron Devices 46 (1999) 525–532.

[4] R. Puthenkovilakam, E.A. Carter, J.P. Chang, First-principles exploration of alternative gate dielectrics: electronic structure of ZrO_2/Si and $ZrSiO_4$/Si interfaces, Physical Review B 69 (2004) 155329.

[5] L.-Z. Hsieh, H.-H. Ko, P.-Y. Kuei, C.-Y. Lee, Growth evolution of ZrO_2 from deposited Zr metal during thermal oxidation, Japanese Journal of Applied Physics 45 (2006) 7680–7681.

[6] H.D. Kim, S.W. Jeong, M.T. You, Y. Roh, Effects of annealing gas (N_2, N_2O, O_2) on the characteristics of $ZrSi_xO_y$/ZrO_2 high-κ gate oxide in MOS devices, Thin Solid Films 515 (2006) 522–525.

[7] Y. Nagasato, T. Aya, Y. Iwazaki, M. Hasumi, T. Ueno, K. Kuroiwa, Low-temperature fabrication of ultrathin ZrO_2/Si structure using metal deposition followed by oxygen annealing, Japanese Journal of Applied Physics 44 (2005) 5–7.

[8] T. Kurniawan, K.Y. Cheong, K.A. Razak, Z. Lockman, N. Ahmad, Oxidation of sputtered Zr thin film on Si substrate, Journal of Materials Science: Materials in Electronics 22 (2011) 143–150.

[9] T. Kurniawan, Y.H. Wong, K.Y. Cheong, J.H. Moon, W. Bahng, K. Abdul Razak, Z. Lockman, H. Joon Kim, N.-K. Kim, Effects of post-oxidation annealing temperature on ZrO_2 thin film deposited on 4H-SiC substrate, Materials Science in Semiconductor Processing 14 (2011) 13–17.

[10] Koyama, K. Suguro, M. Yoshiki, Y. Kamimuta, M. Koike, M. Ohse, C. Hongo, A. Nishiyama, Thermally stable ultra-thin nitrogen incorporated ZrO_2 gate dielectric prepared by low temperature oxidation of ZrN, in: International Electron Devices Meeting, 2001. IEDM Technical Digest., 2001, 20.3.1–20.3.4.

[11] C.H. Chen, Y.K. Fang, C.W. Yang, Y.S. Tsair, M.F. Wang, L.G. Yao, S.C. Chen, C.H. Yu, M.S. Liang, The 1.3–1.6 nm nitrided oxide prepared by NH_3 nitridation and rapid thermal annealing for 0.1 μm and beyond CMOS technology application, Solid-State Electronics 46 (2002) 539–544.

[12] R.M.C. de Almeida, I.J.R. Baumvol, Reaction-diffusion in high-κ dielectrics on Si, Surface Science Reports 49 (2003) 1–114.

[13] S. Dimitrijev, H.B. Harisson, P. Tanner, K.Y. Cheong, J. Han, in: W.J. Choyke, H. Matsunami, G. Pensl (Eds.), "Properties of Nitrided Oxides on SiC," in Silicon Carbide—Recent Major Advances, Springer-Verlag, Berlin, Germany, 2004, pp. 373–386.

[14] Y.H. Wong, K.Y. Cheong, Thermal oxidation and nitridation of sputtered Zr thin film on Si via N_2O gas, Journal of Alloys and Compounds 509 (2011) 8728–8737.

[15] Y.H. Wong, K.Y. Cheong, Electrical characteristics of oxidized/nitrided Zr thin film on Si, Journal of the Electrochemical Society 158 (2011) H1270–H1278.

[16] Y.H. Wong, K.Y. Cheong, Band alignment and enhanced breakdown field of simultaneously oxidized and nitrided Zr film on Si, Nanoscale Research Letters 6 (2011) 489.

[17] Y.H. Wong, K.Y. Cheong, Metal-oxide-semiconductor characteristics of Zr-oxynitride thin film on 4H-SiC substrate, Journal of the Electrochemical Society 159 (2012) H293–H299.

[18] D.K. Schroder, Semiconductor Material and Device Characterization, third ed., Wiley, 2006.

[19] K.Y. Cheong, W. Bahng, N.-K. Kim, Effects of thermal nitrided gate-oxide thickness on 4H silicon-carbide-based metal-oxide-semiconductor characteristics, Applied Physics Letters 90 (2007) 012120.

[20] P. Jamet, S. Dimitrijev, Physical properties of N_2O and NO-nitrided gate oxides grown on 4H SiC, Applied Physics Letters 79 (2001) 323–325.

[21] P. Jamet, S. Dimitrijev, P. Tanner, Effects of nitridation in gate oxides grown on 4H-SiC, Journal of Applied Physics 90 (2001) 5058–5063.

[22] K.Y. Cheong, S. Dimitrijev, J. Han, H.B. Harrison, Electrical and physical characterization of gate oxides on 4H-SiC grown in diluted N_2O, Journal of Applied Physics 93 (2003) 5682–5686.

[23] K.Y. Cheong, J. Moon, H.J. Kim, W. Bahng, N.-K. Kim, Metal-oxide-semiconductor characteristics of thermally grown nitrided SiO_2 thin film on 4H-SiC in various N_2O ambient, Thin Solid Films 518 (2010) 3255–3259.