Available online at www.sciencedirect.com
ScienceDirect
Microelectronics Reliability 47 (2007) 36–40
MICROELECTRONICS RELIABILITY
www.elsevier.com/locate/microrel

Single band electronic conduction in hafnium oxide prepared by atomic layer deposition ☆

Sergey Shaimeev [a], Vladimir Gritsenko [a,*], Kaupo Kukli [b], Hei Wong [c],
Eun-Hong Lee [d], Chungwoo Kim [d]

[a] *Institute of Semiconductor Physics, 630090 Novosibirsk, Russia*
[b] *Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland*
[c] *Department of Electronic Engineering, City U, 83 Tat Chee Avenue, Kowloon, Hong Kong*
[d] *Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Republic of Korea*

Received 17 January 2006; received in revised form 1 March 2006
Available online 5 May 2006

Abstract

Current–voltage and capacitance–voltage measurements on MOS structures with hafnium gate oxide (HfO_2) prepared by atomic layer deposition were conducted to determine the dominant current conduction in the Al/HfO_2/Si structure. In n-type substrate MOS structures, electron injection from Al into HfO_2 is observed when the Al electrode is negatively biased. Whereas in p-type MOS capacitors at negative biasing, no hole injection can be detected and the current in the insulator is again due to the electron injection from Al. These results unambiguously indicate that in both p- and n-type substrates and at both biasing polarities only electronic current conduction in the Si/HfO_2/Al is significant.

1. Introduction

To suppress the direct tunneling current through the gate dielectric in future CMOS devices with channel length less than 70 nm, physically thicker high-κ dielectrics become indispensable. Because of its high chemical stability, wide band gap, high electron and hole barriers at Si/HfO_2 interface, hafnium oxide or hafnia (HfO_2) is recognized as one of the most promising candidates for future CMOS devices and is now intensively investigated [1–5]. The bandgap of HfO_2 is in the range of 5.25–5.8 eV [6–9]. This value is close to the band gap of silicon nitride which is in the range of 4.5–5.3 eV [10]. Unfortunately, hafnia is also similar to silicon nitride in having high trap density [5,11,12]. In addition, several issues still need further investigation before any real applications of hafnia [1,2] become possible. Regarding the current conduction in hafnia, presently there is no enough available data for comparison. It is well known that the conduction of Si_3N_4 in metal–nitride–silicon (MNS) structures is bipolar (two bands). When the metal electrode is positively biased (Si is negatively biased), the conduction current in MNS structure is dominated by the electron injection from silicon. For the metal electrode being negatively biased metal the current conduction is governed by the hole injection from silicon [13–17].

Whereas the current conduction in Si–SiO_2–Al structure is governed by the electronic injection only as the electron barrier at Si/SiO_2 interface (3.14 eV) is substantially smaller than that of the hole barrier (~3.8–4.5 eV). The carrier sign in semiconductors can be determined using Hall, or thermo-power measurements. However, due to the low carrier density in the wide band gap insulator, neither Hall effect nor thermo-power method can be used to determine

---

☆ An earlier version of this paper was published in the Proceedings of the 2005 International Conference on Electron Devices and Solid-State Circuits (EDSSC 2005), Hong Kong, 19–21 December 2005, p. 703–6.

[*] Corresponding author.
E-mail address: grits@isp.nsc.ru (V. Gritsenko).

0026-2714/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.microrel.2006.03.002

the carrier sign. The carrier sign in Si_3N_4 was determined by using the minority carrier injection from n- and p-type silicon [14–17]. This method was confirmed with a complicated method based on carrier separation technique using field effect transistor [13]. The sign of carrier conduction is important because it governs the carrier injection and charge trapping which give rise to the instability of threshold voltage of MOS transistors. The objective of this paper is to determine the dominant carrier sign in hafnium oxide using minority carrier injection from n- and p-type silicon substrate in MOS (Si–HfO_2–Al) structures. The hafnium oxide was prepared by atomic layer deposition (ALD). ALD method has been demonstrated to be a promising one for HfO_2 thin film fabrication. It is a process with self-limit and conformal growth and with excellent thickness and composition uniformities [5].

2. Experiments

The HfO_2 films used in this investigation were grown in a hot-wall horizontal flow-type F120 ALD reactor [18]. The hafnium precursor $HfCl_4$ was evaporated from an open boat at 160 °C inside the reactor. The pulse length of $HfCl_4$ was 400 ms while the pulse length of water and purging periods were 500 ms. Nitrogen was used as the precursor carrier as well as the purge gas. The pressure in the reactor was about 10 mBar. H_2O vapor, generated in an external reservoir at room temperature, was led into the reactor through needle and solenoid valves to deposit the hafnium oxide

HfO_2 films were grown at 300 °C on p-Si or n-Si substrate with ⟨100⟩ orientation and resistivity of 5–7 Ω cm. Prior to the deposition, the native SiO_2 layer was removed by etching the substrates in 1% HF aqueous solution for 25–30 s. The film thickness was evaluated by fitting the optical reflection spectra [19] from a Hitachi U2000 spectrophotometer and is 70 nm and 57 nm for p-type substrate and n-type substrate, respectively. The crystallinity of the as-deposited thin films was evaluated by grazing incidence diffractometry (GIXRD) using a Bruker D8 Advance X-ray diffractometer.

To carry out the electrical measurements, aluminum electrodes with effective area of 0.204 mm^2 were e-beam evaporated on the as-deposited hafnia film. The backside of the silicon wafer was etched in hydrofluoric acid and ohmic contact was created by depositing Al after the etching. Capacitance–voltage (*C–V*) measurements were conducted at a frequency of 100 kHz and the current–voltage (*I–V*) measurements were performed using a ramp voltage with a rate of 0.15 V/s. All measurements were made at room temperature.

3. Results and discussion

The films grown from $HfCl_4$ and H_2O at 300 °C can be described approximately as stoichiometric dioxides [18]. The contents of residual chlorine and hydrogen are not higher than 1.0 at.% and 0.4 at.%, respectively in the obtained films. The films were polycrystalline and consist of monoclinic HfO_2 phase (Fig. 1). As depicted in Fig. 1, a diffraction peak from additional tetragonal HfO_2 could be detected at 30.4°. It has been shown that the contribution from tetragonal or cubic metastable phases, as well as the amorphous regions, increase for thinner films [18,20]. Thus phase inhomogeneity is expected in our thicker films. Moreover, the layers at the oxide/silicon interface, as well as the topmost oxide layer, containing more impurities and having less defined lattice parameters, are likely to be more disordered when compared to the bulk material. Therefore, the films used in this investigation are defective in terms of both impurity content and polycrystallinity.

Fig. 2 shows energy diagram of p-Si/HfO_2/Al MOS structure at: (a) zero biasing, (b) positive biasing (applying positive voltage to Al contact), and (c) negative biasing. Capacitance–voltage and current–voltage characteristics were measured and the results are depicted in Fig. 3(a) and (b), respectively. At positive biasing (depletion mode), the current rises exponentially as the biasing voltage increasing up to 1.5 V. At higher voltage, the current tend to be saturated. At positive biasing, the capacitance decreases from the inversion value to the depletion capacitance value. Both current saturation and capacitance reduction are related to the out-flowing of the minority carriers (electrons) from the silicon substrate to the gate dielectric. The finite minority carrier generation in the space charge region of Si surface results in the expansion of depletion layer and in a larger voltage drop across this layer (see Fig. 2(b)). Further confirmation of the substrate electron injection was obtained with illumination experiments. As shown in Fig. 3, illumination results in the increase of saturation current and depletion capacitance (see Fig. 3(a) and (b)) because of additional minority carrier (electron) generation in depletion region. Similar substrate electron injection in positively based metal was also observed in metal/nitride/oxide/silicon (MNOS) structures

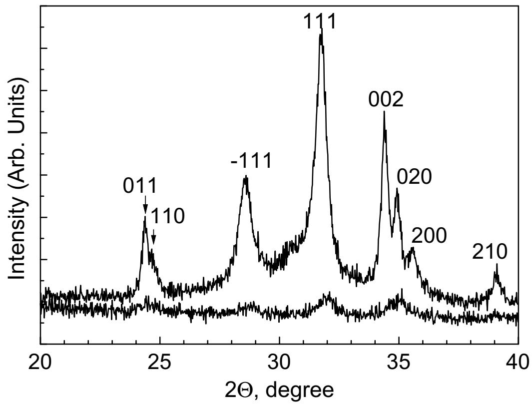

Fig. 1. Typical grazing incidence X-ray diffraction patterns of HfO_2 films grown on Si(100) substrates. The X-ray incidence angle is 0.3° for bottom trace and 1.0° for upper trace. The diffraction peaks are assigned as those of monoclinic polymorph HfO_2.

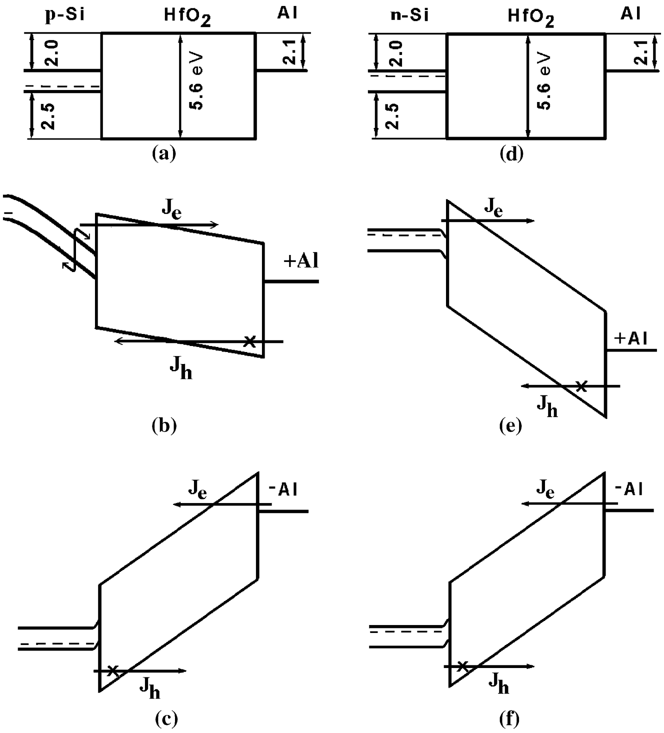

Fig. 2. Energy diagram of Si/HfO$_2$/Al structures with p-type substrate (a)–(c) and n-type substrate (d)–(f). Biasing conditions: (a) and (d) without biasing; (b) and (e) positive voltage is connected to the metal; (c) and (f) negative voltage is connected to the substrate.

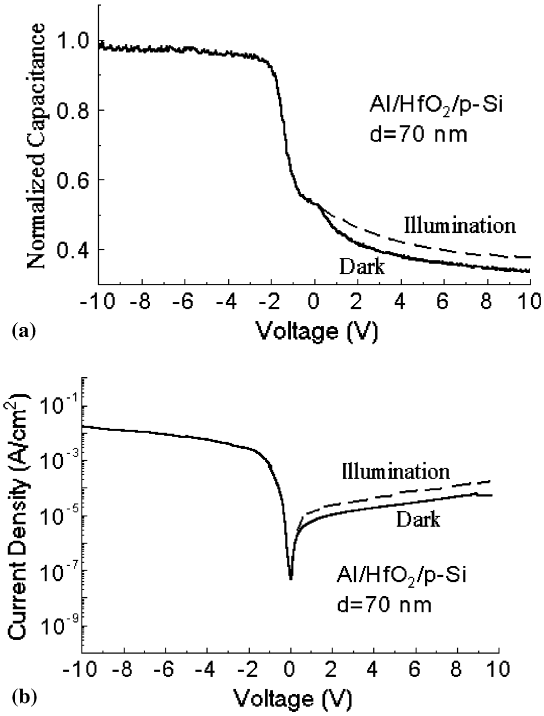

Fig. 3. (a) Capacitance–voltage and (b) current–voltage characteristics of p-Si/HfO$_2$/Al structures. The thickness of HfO$_2$ is 70 nm. The voltage polarity is referred to the gate electrode.

with thin (∼2 nm) tunnel oxide [14–17] and in metal/nitride/silicon (MNS) structures with boron nitride (BN) [21]. The current saturation and capacitance reduction in the present experiments unambiguously imply that when the metal is positively biased the current conduction should be due to the electron injection from the silicon into the hafnium oxide. The value of electron barrier at the Si/HfO$_2$ interface, determined by photoemission measurements, is 2.0 eV [6]. Regarding the band gap value of HfO$_2$, there are several different published values. Depending on the sample preparation methods, the gap determination methods and the model used for experimental data interpretation, the band gap value is found to be in the range 5.22–5.8 eV [6–9]. We used the latest value of 5.6 eV reported by Afanas'ev, Stesmans and Tsai [8]. The electron barrier at Al/HfO$_2$ interface measured with photoemission method is 2.1 eV [6]. Based on these data, a detailed band diagram of the Si/HfO$_2$/Al structure can be determined and is shown in Fig. 2(a). As can be seen in Fig. 2(a), the electron barrier at Si/HfO$_2$ interface is lower than the hole barrier (3.5 eV) at the Al/HfO$_2$ interface. Hence the hole injection from Al electrode is not likely to occur. Similar argument can be applied to that case of negatively metal in MOS structure biased on p-type substrate. The leakage current is governed by the electron injection from Al into HfO$_2$ (see Fig. 2(c)). In addition, since the hole barrier at Si/HfO$_2$ interface (2.5 eV) is larger than the electron barrier at Al/HfO$_2$ interface (2.1 eV), the current conduction will be dominated by the electron injection from the metal instead of hole injection from silicon when the Al is negatively biased.

Fig. 4 shows the capacitance–voltage and current–voltage characteristics of n-Si/HfO$_2$/Al structure. When the metal is positively biased (accumulation), all applied voltage will drop on the dielectric and the current increases exponentially as the voltage increases (Fig. 4(b)). In that case, the current conduction is again electronic, and is due to the electron injection from Si into HfO$_2$. The *C–V* hysteresis in Fig. 4(a) confirms this allegation. As shown in Fig. 4(a), when a positive voltage (+15 V) was applied to the gate electrode, a flatband voltage shift of 9 V to positive voltage was observed. This behavior indicates that a negative charge (electron) accumulation in HfO$_2$ occurs, due to the electron injection from Si. When −15 V is applied to the Al electrode, the flat band voltage shift in the *C–V* curves is about +7 V. The electron trap concentration estimated from the *C–V* hysteresis is about 10^{19} cm^{-3}. When the metal is negatively biased, neither capacitance depletion nor current saturation can be recorded. Current value in inversion does not depend on the illumination in this case. These results again indicate that the conduction of hafnium oxide at negatively biased Al is not a result of the minority carrier (hole) injection from silicon. The current conduction in this case is due to the electron injection from aluminum.

The charge transport mechanism in MOS structure with thin HfO$_2$ as gate dielectrics was studied by Zhu et al. [22]. We are not going to investigate the charge transport mechanism again. Since the electron barrier at Si/HfO$_2$

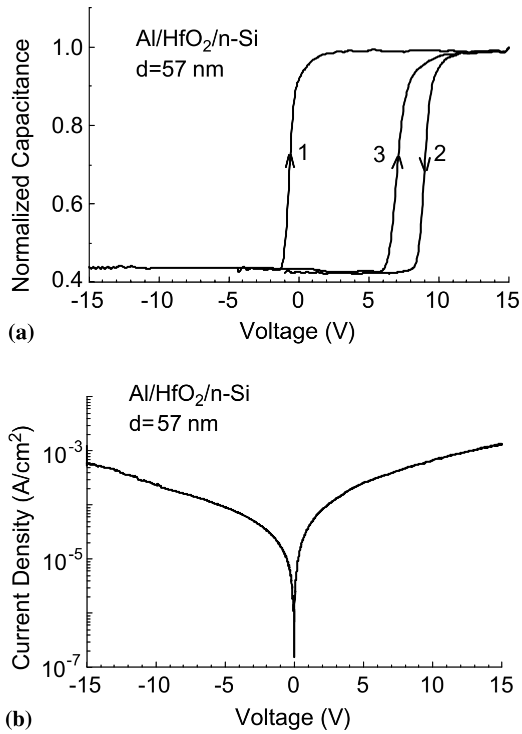

Fig. 4. (a) Capacitance–voltage (a) and (b) current–voltage characteristics of n-Si/HfO$_2$/Al structure with HfO$_2$ thickness of 57 nm. In *C–V* measurement, curve 1 (initial) is measured with voltage sweep from −5 V to +15 V, curve 2 from +15 V to −15 V, curve 3 from −15 V to +15 V. Voltage polarity is referred to the gate electrode.

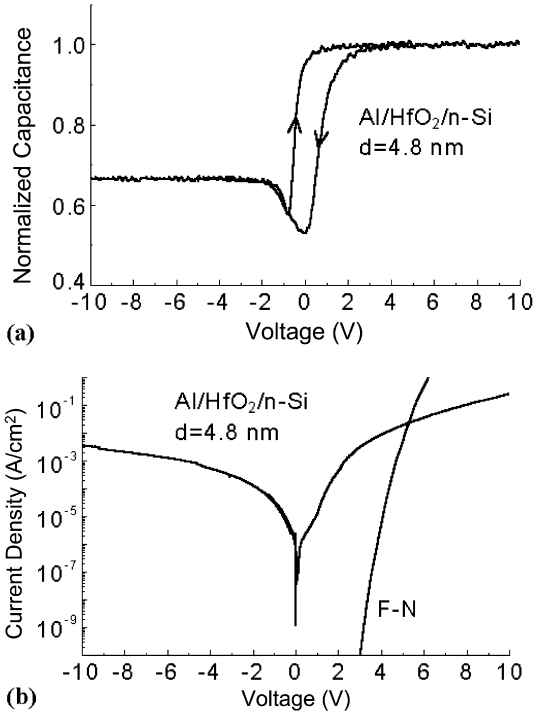

Fig. 5. (a) Capacitance–voltage and (b) current–voltage characteristics of n-Si/HfO$_2$/Al structures with thin HfO$_2$ thickness of 4.8 nm. F–N curve in (b) is the theoretical Fowler–Nordheim plot with barrier height of 2.0 eV. The voltage polarity is referred to the gate electrode.

and at Al/HfO$_2$ is about 2 eV, the current should be limited by Fowler–Nordheim (F–N) injection from the contacts. Fowler–Nordheim conduction is described by

$$J = AF^2 \exp[-B(m^* \phi^{3/2}/F]$$
$$A = q^3/(8\pi h\phi), \quad B = 8\pi\sqrt{2}/3hq \tag{1}$$

where F is the electric field strength, ϕ is the barrier height and m^* is effective mass of the tunneling electron.

When calculated the F–N electron current from Si with barrier height of 2.0 eV and effective electron mass $m^* = 0.5m_o$ [23], the obtained value of the tunnel current at low electric fields ($V < 5.5$ eV) is substantial lower than the experimental findings (see Fig. 5(b)). High leakage current in HfO$_2$ MOS structures was observed in other works [4,22]. One possible explanation for the high current leakage in MOS structures with hafnia gate oxide may be the trap-assisted electron injection mechanism from the contact [24]. Grain boundary conduction due to the polycrystalline dielectric film is another possible leakage mechanism [25]. Further experimental work is needed to confirm the proposed mechanisms.

4. Conclusions

In summary, hafnium oxide films were prepared by atomic layer deposition. The study of the current conduction polarity, capacitance–voltage and current–voltage measurements on the Si/HfO$_2$/Al structures were performed. Both n-type and p-type Si substrates were used. Unlike the two band conduction in MIS structures with Si$_3$N$_4$ and boron nitride as gate dielectrics, the current conduction in HfO$_2$ MOS capacitors is governed by the electron injection only, regardless of the biasing polarities and the type of substrate doping. This single band electronic current conduction behavior is more similar to the case of MOS structures with thermal silicon oxide. Further exploration is needed in order to clarify the pronounced excess leakage current over the Fowler–Nordheim mechanism.

Acknowledgements

The authors would like to thank K. A. Nasyrov of Institute of Autometry, Novosibirsk, Russia, for helpful discussion and Dr. V. Filip of City University of Hong Kong for proofreading. This work was supported by project no:116 of Siberian branch of Russian academy of sciences, project no. 7001790 funded by City University of Hong Kong, and particular by National Program for Tera-Level Nanodevice of the Korea Ministry of Science and Technology as one of the 21st Century Frontier Programs.

References

[1] Wilk GD, Wallace RM, Anthony JM. High-k gate dielectrics: current status and materials properties considerations. J Appl Phys 2001;89:5243–7275.

[2] Gutowski M, Jaffe JE, Liu CL, Stoker M, Hegde RI, Rai RS, et al. Thermodynamic stability of high-K dielectric metal oxides ZrO_2 and HfO_2 in contact with Si and SiO_2. Appl Phys Lett 2002;80:1897–9.

[3] Gusev EP, Cartier E, Buchanan DA, Gribelyuk M, Copel M, Okorn-Schmidt H, et al. Ultrathin high-k metal oxide on silicon: processing, characterization and integration issues. Microelectron Eng 2001; 59:341–9.

[4] Zhan N, Ng KL, Poon MC, Kok CW, Wong H. XPS study of the thermal instability of hafnium oxide prepared by Hf sputtering in oxygen with rapid thermal annealing. J Electrochem Soc 2003; 150:F200–2.

[5] Sundqvist J, Hastra A, Aarik J, Kukli K, Aida A. Atomic layer deposition of polycrystalline HfO_2 films by the HfI_4–O_2 precursor combination. Thin Solid Films 2003;427:147–51.

[6] Afanas'ev VV, Stesmans A, Chen F, Shi X, Campbell SA. Internal photoemission of electrons and holes from (100) Si into HfO_2. Appl Phys Lett 2002;81:1053–5.

[7] Yu HY, Li MF, Cho BJ, Yeo CC, Joo MS, Kwong D-L, et al. Energy gap and band alignment for $(HfO_2)_x\,(Al_2O_3)_{1-x}$ on (100) Si. Appl Phys Lett 2002;81:376–8.

[8] Afanas'ev VV, Stesmans A, Tsai W. Determination of interface energy band diagram between (100)Si and mixed Al–Hf oxides using internal electron photoemission. Appl Phys Lett 2003;82:245–7.

[9] Schaeffer J, Edwards NV, Liu R, Roan D, Hradsky B, Gregory R, et al. H_2O gate dielectric deposited via tetrakis diethylamido hafnium. J Electrochem Soc 2003;150:F67.

[10] Gritsenko VA. Electronic structure and optical properties of silicon nitride. Silicon nitride in electronics. New York: Elsevier; 1986.

[11] Lee BH, Kang L, Nieh R, Qi W-J, Lee JC. Thermal stability and electrical characteristics of ultrathin hafnium oxide gate dielectric reoxidized with rapid thermal annealing. Appl Phys Lett 2000; 76:1926–8.

[12] Wong H, Ng KL, Zhan N, Poon MC, Kok CW. Interface bonding structure of hafnium oxide prepared by direct sputtering of hafnium in oxygen. J Vac Sci Technol B 2004;22:1094–100.

[13] Ginovker AS, Gritsenko VA, Sinitsa SP. Two band conduction of amorphous silicon nitride. Phys Stat Sol B 1974;26:489–95.

[14] Hielscher FH, Preier HM. Non-equilibrium *C–V* and *I–V* characteristics of metal–insulator–semiconductor capacitors. Solid-State Electron 1969;12:527–38.

[15] Ginovker AS, Gritsenko VA, Sinitsa SP. Stationary current in MNOS structures. Microelectronics 1973;2:283–9 (in Russian).

[16] Gritsenko VA, Meerson EE. On silicon nitride conductivity. Phys Stat Sol A 1980;62:K131.

[17] Buchanan DA, Abram RA, Morant MJ. Charge trapping in silicon-rich Si_3N_4 films. Solid-State Electron 1987;30:1295–301.

[18] Kukli K, Ritala M, Sajavaara T, Keinonen J, Leskelä M. Comparison of hafnium oxide films grown by atomic layer deposition from iodide and chloride precursors. Thin Solid Films 2002;416: 72–9.

[19] Ylilammi M, Ranta-aho T. Optical determination of the film thickness in multilayer thin film structures. Thin Solid Films 1993; 232:56–62.

[20] Kukli K, Ritala M, Leskelä M, Sajavaara T, Keinonen J, Gilmer DC, et al. J Mater Sci: Mater Electr 2003;14:361.

[21] Voskoboinikov VV, Gritsenko VA, Efimov VM, Lesnikovskaja VE, Edelman FL. Structure and electrophysical properties of boron nitride thin films. Phys Stat Sol A 1976;34:85–94.

[22] Zhu WJ, Ma T-P, Tamagawa T, Kim J, Di Y. Current transport in metal/hafnium/oxide/silicon structure. IEEE Electron Device Lett 2002;23:97–9.

[23] Gritsenko VA, Meerson EE, Morokov YuN. Thermally assisted tunneling at Au–Si_3N_4interface and energy band diagram of metal-nitride-oxide-semiconductor structures. Phys Rev B 1997;57:R2081–R2083.

[24] Wong H, Cheng YC. Electronic conduction mechanism in thin oxynitride films. J Appl Phys 1991;70:1078–80.

[25] Wong H, Han PG, Poon MC. Study of grain boundary tunneling in barium titanate ceramic films. J Korean Phys Soc 1999;35: S196–S199.