

## Reduced Interfacial Layer Thickness and Gate Leakage Current of ALD Grown HfAlO<sub>3</sub> with TaN Gates using Chemical Oxides and Spike-Annealing

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### I. INTRODUCTION

According to the ITRS, the thickness of gate oxide in 2007 will be reduced to 1.1nm. However, the nm-scale SiO<sub>2</sub> thin film increases leakage current drastically and cannot be used because of large power dissipation. In recent years, high-k dielectric has obtained much attention to replace SiO<sub>2</sub> gate insulator for the applications of ULSI [1][2]. Then, high gate capacitance or low equivalent oxide thickness thus can be achieved simultaneously with low gate currents. One of the most promising deposition techniques for high-K materials is atomic layer deposition (ALD), since it is manufacturable and provides excellent conformality and uniformity [3][4]. In ALD, materials are deposited layer by layer in a self-limiting fashion, allowing for inherent atomic scale control. The most widely used ALD precursors for metal oxides are metal-chlorides, such as HfCl<sub>4</sub> and Al(CH<sub>3</sub>)<sub>3</sub>. Unfortunately, metal oxide formed by a ALD using metal chloride precursors exhibits poor initial deposition on H-terminated Si[5][6], necessitating the use of an interfacial SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> layer to achieve uniform growth. However, the interfacial layer between the high-K layer and silicon substrate can have an opposing effect on this pursuit of low effective oxide thickness (E<sub>OT</sub>) and low gate currents. Since an E<sub>OT</sub> of less than 1 nm will soon be required, the need for an initial few monolayers of a lower dielectric constant material would be a serious drawback.

Interfacial SiO<sub>2</sub> layers are conventionally produced by the thermal oxidation at temperatures above 800 °C in O<sub>2</sub> or N<sub>2</sub>O. The high performance of MOS devices relies on almost perfect characteristics of the Si/SiO<sub>2</sub> interfaces. However, the serious problem is that the control of the SiO<sub>2</sub> thickness becomes very difficult because of the high Si oxidation rate at high temperatures.

In the present study, we will discuss the chemical oxide formed in HNO<sub>3</sub>, SCl, and H<sub>2</sub>SO<sub>4</sub>. A high temperature spike annealing treatment is performed to decrease the chemical oxide thickness and then use it as the interfacial layer of high K dielectric. Characteristics of the gate stack of TaN/HfAlO<sub>3</sub>/chemical oxide/Si are also compared and discussed, simultaneously.

### II. Device Fabrication

The starting material was wafer of 6-in Si (100) with 15~25 Ω-cm, and it was clean using RCA methods. The first group samples are MOS devices with TaN/ SiO<sub>2</sub>/Si structures. Gate dielectric was performed by immersing wafers in to chemical solutions (HNO<sub>3</sub>, NH<sub>4</sub>OH+H<sub>2</sub>O<sub>2</sub> (SCl), and H<sub>2</sub>SO<sub>4</sub>). After the formation of chemical oxide layers, TaN layer was carried out in PVD system for gate electrode, and then annealed by RTA at 850 °C for 30-sec.

The second group samples are MOS devices with TaN/HfAlO<sub>3</sub>/chemical oxide/Si structures. Gate dielectric was performed by immersing wafers into nitric acid solutions following by various spike-annealing (1000 °C, and 1050 °C). Then, the HfAlO<sub>3</sub> films were grown by the ALD process, by alternating pulses of HfCl<sub>4</sub>, H<sub>2</sub>O and Al(CH<sub>3</sub>)<sub>3</sub> at 300 °C. TaN layer was carried out in PVD system for gate electrode, and then annealed by RTA at 850 °C for 30-sec. Finally, Al was deposited on the backside by sputtering, and PMA treatment was performed at 400 °C in forming gas atmosphere. I-V characteristics were measured using an HP 4145 picoammeter. C-V curves, which operating frequency is 100K, were recorded with a HP4284

### III. Results and Discussion

Fig. 1 shows the C-V and hysteresis curves for the TaN/ chemical SiO<sub>2</sub> /Si(100) with the SiO<sub>2</sub> layer formed in HNO<sub>3</sub>, SCl, and H<sub>2</sub>SO<sub>4</sub>, respectively. At the same immersion process time, the HNO<sub>3</sub> depicts

the highest capacitance value among all splits. The hysteresis, which may limit the application because the hysteresis leads to instability of threshold voltage of MOSFETs, was defined as a difference between flat band voltages of C-V curves swept from V to -2.5 V and vice versa. From Fig. 1, the hysteresis voltage is found to be 137 mV for H<sub>2</sub>SO<sub>4</sub> split, 75 mV for SCl split, and there is almost no difference for HNO<sub>3</sub> split.

Table I shows the oxide thickness, J<sub>g</sub> (at V-V<sub>FB</sub>=-1V) for the three different chemical oxides. It is interesting that HNO<sub>3</sub> splits have the lowest oxide thickness and J<sub>g</sub>. Fig. 2 shows the C-V curves for MOS devices with TaN/HfAlO<sub>3</sub>/chemical SiO<sub>2</sub> /Si(100). The interfacial SiO<sub>2</sub> layer was formed in HNO<sub>3</sub>, and then annealed by high temperature spiking anneal (1000 °C, and 1050 °C). From Fig. 2, the E<sub>OT</sub> and also donor-like interface state are reduced after high temperature spiking anneal as compared with ideal simulation results[7]. To compare the interfacial layer between W/ and W/O spiking anneal, high-resolution TEM pictures of TaN/ HfAlO<sub>3</sub> /chemical SiO<sub>2</sub> /Si(100) were analyzed. Fig. 3 shows TEM pictures for interfacial layer after spiking anneal in nitrogen ambient. Note that the splits with 1000 °C (Fig. 3(b)), and 1050 °C (Fig. 3(b)) spike anneal show thinner physical thickness, which was from 1nm for W/O anneal (Fig. 3(a)) to 0.7 nm for 1000 °C, and 1050 °C spike anneal. Therefore, HNO<sub>3</sub> chemical oxide could be effectively reduced by high temperature spike anneal. Fig. 4 shows the C-V and hysteresis curves for the TaN/ HfAlO<sub>3</sub> /chemical SiO<sub>2</sub> /Si samples with (a) control (b) spiking anneal at 1050 °C. There is almost no hysteresis difference for HNO<sub>3</sub> splits with or W/O high temperature anneal. Therefore, instability of threshold voltage could be ignored.

Fig. 5 shows gate leakage currents-voltage characteristics. The splits with high temperature spike anneal show higher gate current due to its thinner interfacial oxide thickness. However, the leakage current was suppressed around gate voltage around 0 V. This is because the interface states were suppressed after spike anneal. Fig. 6 shows stress induced leakage current (SILC) characteristics of the TaN/ HfAlO<sub>3</sub> /chemical SiO<sub>2</sub> /Si. SILC is defined as the increase in leakage current after stress {J<sub>g</sub>(T)-J<sub>g</sub>(0)} divided by leakage current of a fresh device (J<sub>g</sub>(0)). Compared to the splits W/O spike anneal, negligible SILC for the splits with high temperature spike anneal is observed.

### IV. Summary

Chemical oxidation of Si by different chemical is investigated in view of its application to gate oxides. HNO<sub>3</sub> oxide shows the thinnest gate oxide and lowest leakage current among all chemical oxide splits. Furthermore, the method of high temperature spike anneal not only reduce the thickness of HNO<sub>3</sub> chemical oxide, but also suppress the gate leakage current and SILC due to reduced donor-like interface traps.

### Reference:

- [1] S. J. Lee, et al., VLSI Symp. Tech. Dig., (2001), p. 133.
- [2] T. Iwamoto, et al., IEDM Tech Dig., (2003), p. 639.
- [3] Heyns, et al., VLSI Technology, Systems, and Applications, 2003 International Symposium (2003), p.247.
- [4] J.F. Conley, et al., Electrochem. and Sol. State Lett. (2002)
- [5] M. Couel, et al., Phys. Lett. **76**, 436 (2000).
- [6] M. Tuominen, et al., In Electrochemical Society Proceedings Vol. 2000-9, 11. 271-82 (2000).
- [7] H. Fujioka, et al., "QMCV simulator," online available <http://www-device.eecs.berkeley.edu/qmcv/index.shtml>

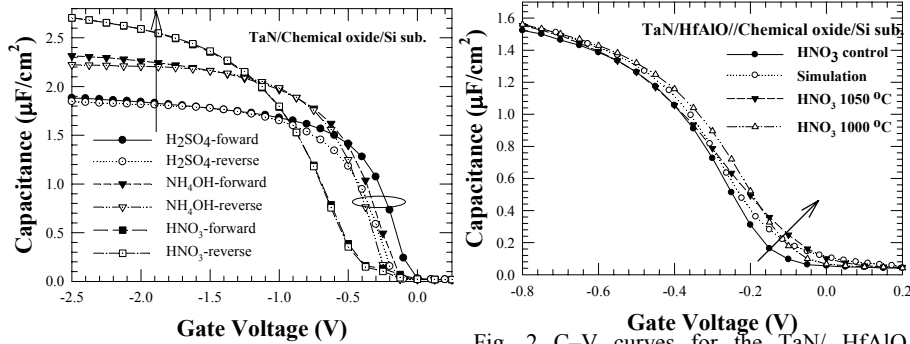


Fig. 1. C-V and hysteresis curves for the TaN/ chemical SiO<sub>2</sub> /Si(100) with the SiO<sub>2</sub> layer formed in HNO<sub>3</sub>, SCI, and H<sub>2</sub>SO<sub>4</sub>, respectively.

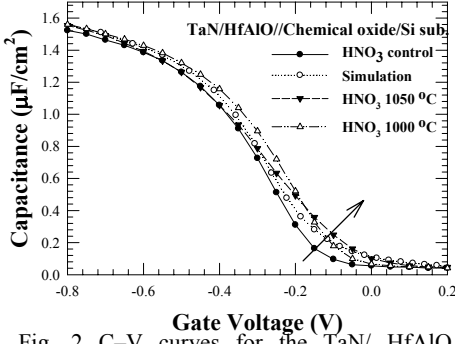


Fig. 2 C-V curves for the TaN/ HfAlO /chemical SiO<sub>2</sub> /Si(100). The interfacial SiO<sub>2</sub> layer formed in HNO<sub>3</sub>, and then annealed by high temperature spiking anneal (1000 °C, and 1050 °C).

Sample	Chemical oxide	EOT	J <sub>g</sub> (A/cm <sup>2</sup> ) at V-V <sub>FB</sub> =-1 V
1	H <sub>2</sub> SO <sub>4</sub>	14.5Å	6.212
2	SCI	10.5Å	11.815
3	HNO <sub>3</sub>	9Å	4.2881

Table I. Oxide thickness, J<sub>g</sub> (at V-V<sub>FB</sub>=-1V) for the three different chemical oxide.

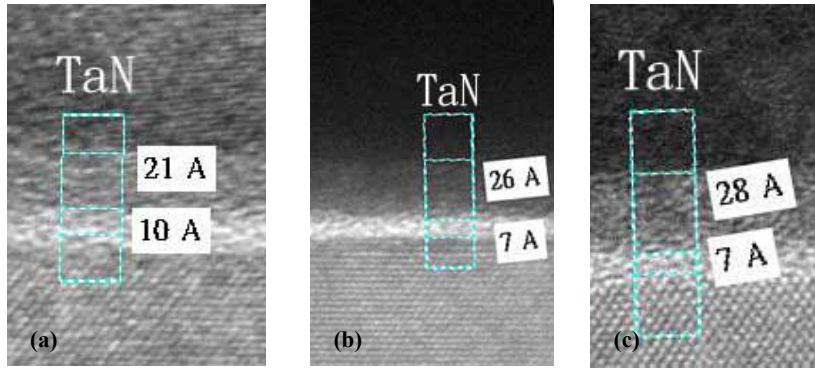


Fig. 3 TEM pictures for interfacial layer, (a) Control sample: W/O anneal (b) Spike anneal: 1000 °C (c) Spike anneal: 1050 °C

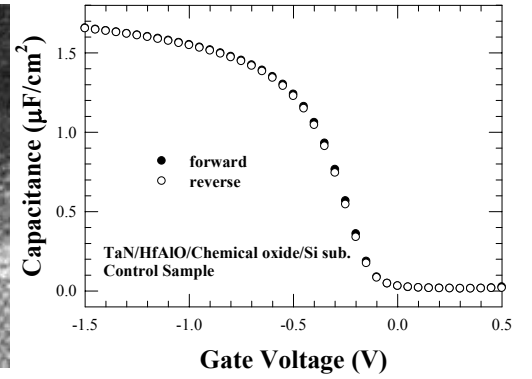


Fig.4(a). C-V and hysteresis curves for the TaN/ HfAlO /chemical SiO<sub>2</sub> /Si control sample.

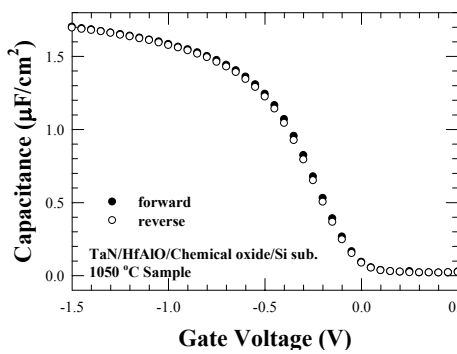


Fig.4(b). C-V and hysteresis curves for the TaN/ HfAlO /chemical SiO<sub>2</sub> /Si sample with 1050 °C spiking annealing.

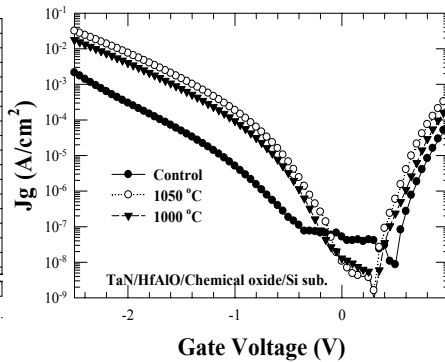


Fig.5. Gate leakage currents versus voltage characteristics for all split samples.

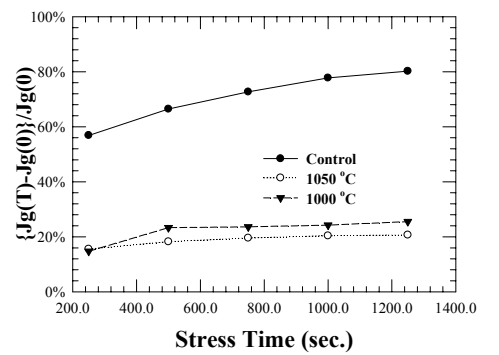


Fig.6. SILC characteristics of the TaN/ HfAlO /chemical SiO<sub>2</sub> /Si(100). SILC is defined as the increase in leakage current after stress {J<sub>g</sub>(T)-J<sub>g</sub>(0)} divided by leakage current of a fresh device (J<sub>g</sub>(0)).