# The Characterization of HfO<sub>2</sub> Thin Film Treatment by N<sub>2</sub>O

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Abstract — The physical and electrical characteristics of hafnium oxide (HfO<sub>2</sub>) in MOS capacitors with various annealing gas and annealing conditions were investigated. The results show that hafnium oxide with N2O annealing samples has best reliability than other ones. Besides, it is shown that HfO<sub>2</sub> with N<sub>2</sub>O annealed sample has thicker thickness and smaller dielectric constant compared with other annealing conditions. This result may be contributed to that ionic oxygen penetrate through HfO<sub>2</sub> films and react with silicon substrate. This can be found in cross-section TEM picture. In the above discussions, HfO<sub>2</sub> is indeed an alternative gate dielectric for future VLSI gate applications for gate oxide < 12Å or below process.

*Index Terms*—High-K materials,N<sub>2</sub>O anneal, hafnium oxide.

# I. Introduction

. According to 1999 ITRS roadmap, for beyond 0.1  $\mu$  m technology, ultra thin gate oxide with EOT of less than 12 Å are needed. [1] However, SiO<sub>2</sub> is facing the scaling limitation due to direct tunneling current that limits low power application and reliability problems [2-3].

Key issues related to the development of high-K gate dielectric material are thermal stability of high-K materials in direct contact with silicon and poly-Si at high temperatures, high quality interfaces with channel and gate electrode, reasonable barrier height to achieve low leakage current, and suppressed boron penetration.

Recently,  $HfO_2$  films have emerged as the promising gate dielectric due to its dielectric constant of up to 40, energy gap of 5.65eV, and thermodynamically stable when in contact with Si. [4]

In this work, we used  $HfO_2$  as gate dielectric material of capacitor and then annealed with  $N_2O$  and  $N_2$ . Besides, we investigated the mechanism of  $N_2O$  and  $N_2$  annealing for different temperature and time of  $HfO_2$  gate dielectric material.

#### **II. Experimental**

For this research, silicon wafers were cleaned and different physical thickness (80 and 100 Å) of HfO<sub>2</sub> were deposited by reactive sputtering method. Then these samples were annealed using Rapid Thermal annealing methods with different ambient (N<sub>2</sub> and N<sub>2</sub>O) for different time (15, 30, 45 and 60 seconds) and different temperatures (800, 850 and 900°C). Finally, gold and Alumni were chosen for top and back side electrodes, respectively. Control samples were also fabricated by Rapid Thermal N<sub>2</sub>O oxidation (RTN<sub>2</sub>O) with the same oxidation conditions compared with HfO<sub>2</sub> ones. We use HP4285 for capacitor-voltage high frequency measurement and HP4195 for current-voltage measurement. The results were shown in Fig1 and 2.



Fig.1 J-V Characteristics of  $850^{\circ}$ C anneal for different anneal time (15 sec, 30 sec, 45 sec and 60 sec with N<sub>2</sub>O) T<sub>HfO2</sub>=80A



Fig.2 High Frequency C-V for different anneal conditions.

## **III. Results and Discussion**

Fig.3 shows the equivalent oxide thickness (EOT) for different annealing processes. The EOT is calculated from the formula

$$EOT = \frac{\varepsilon_{ox}\varepsilon_0}{\frac{C}{A}}$$

And in those formulas,  $\varepsilon_{ox}$  is the relative dielectric constant of SiO<sub>2</sub>, usually is the value of 3.9,  $\varepsilon_0$  represents the dielectric constant in vacuum, and is the value of 8.85 e-14 F/cm, C is the accumulation capacitor after C-V measurement by HP 4285, A is pattern area.





From the data shown above, we observed that

EOT increases with increasing temperature and anneal time. This is due to that ionic oxygen penetrate through  $HfO_2$  layer and react with Si substrate to form a interface layer between  $HfO_2$  and silicon substrate. The cross-sectional TEM picture of Fig.4 also confirms this phenomenon.



Fig.4 TEM picture of  $HfO_2$  gate dielectric capacitor. The interfacial layer is seen obviously.

At the same time, we also extracted dielectric constant by the method :

$$DielectricCons \tan t = \frac{3.9 \times (Phy_1 - Phy_2)}{EOT_1 - EOT_2}$$

And at here,  $Phy_1$  and  $Phy_2$  stands for two different physical thickness of  $HfO_2$  layer after annealing.  $EOT_1$  and  $EOT_2$  are two different equivalent oxide thickness, respectively. When using this formula, we have an assumption : it supposed that the interfacial layer over whole dielectric and after annealing is not changed. In this way, we have dielectric constant approach to ideal value 30.

Fig.5 shows for that the dielectric constant after higher temperature is lower than that under lower temperature anneal. That is due to at higher temperature anneal, there will grow thicker interfacial layer with lower dielectric constant (<10), therefore, the dielectric constant of higher temperature annealing will be lower.



Fig.5 Dielectric Constant v.s annealing time for different annealing temperatures

Fig.6 shows that the leakage current density compared with three different gate dielectric:  $HfO_2$  gate dielectric annealed with N<sub>2</sub>O and N<sub>2</sub>, and RTN<sub>2</sub>O oxidation SiO<sub>2</sub> gate dielectric. From the plot, we can find that the leakage current density of RTN<sub>2</sub>O oxidation SiO<sub>2</sub> gate dielectric is of the order of 1E-6, for HfO<sub>2</sub> gate dielectric annealed with N<sub>2</sub>O and N<sub>2</sub> are 1E-8 and 1E-7 respectively. From our earlier discussion, lower leakage current means lower trap density and higher physical thickness. We compare with HfO<sub>2</sub> dielectric and RTN<sub>2</sub>O dielectric, the leakage current of HfO<sub>2</sub> dielectric is lower, then there we may use it as future gate dielectric.



Fig.6 Leakage current with different gate dielectric.

#### **IV. Conclusion**

Several findings are present at below :

 Gate leakage current of HfO<sub>2</sub> gate dielectric is smaller than that of RTN<sub>2</sub>O gate dielectric for about 1-2 orders with proper anneal conditions.

(2) After proper annealing conditions, breakdown field of  $HfO_2$  gate dielectric can be larger than  $SiO_2$  gate dielectric.

From above discussions, we can conclude that  $HfO_2$  has several advantages such as low leakage current, larger breakdown field and good dielectric strength. That means  $HfO_2$  is indeed an alternative gate dielectric for future VLSI gate applications for gate oxide <12Å or below process.

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