Chapter 3

Investigation of Surface Treatments Prior to Al_2O_3 Gate Dielectric Deposition

3.1 Introduction

Recently, many high-k materials have been invested intensively. As recent reports, most of high-k materials have higher interface states and poor thermal reliability. As metal gate materials directly contact on Si substrates, the formation of oxide and silicide must be avoided ($MO_X+Si \rightarrow M+SiO_2$ or $MO_X+Si \rightarrow MSiy+SiO_2$). The interface issues at high-k/Si interface will cause the low carrier mobility and degrade the device performance. The SiO_2 or SiO_2-like interfacial layer is applied to improve the interface quality. The interfacial layer would degrade the benefit of high-k materials. The interfacial states may cause large leakage current. Surface roughness scattering would lead to mobility degradation. Therefore, the property of interface at high-k/Si is a critical factor for high-k process.

Traps, dangling bonds and voids [27, 28] are embedded in the transition layer of silicon dioxide. The defects lead to increase of tunneling current and easier induced dielectric breakdown. The interfacial stoichiometry is controlled by the complex combination of oxidation methods, growth kinetics, and equilibrium energies. To avoid the dangling bonds which result in electrically active traps at the interface, the transition region between Si and SiO_2 must be reduced and minimized. Many studies had been demonstrated to enhance oxide quality by various oxidation processes.

To suppress the interfacial layer thickness and maintain excellent transport properties, surface passivation on silicon is necessary. Nitridation is the general method adopted in surface treatments. Nitridation of the silicon surface using NH_3 treatment at 800°C for 1 hour. NH_3 treatment shows the low EOT, preventing boron penetration, oxygen and H_2O suppression, higher interface charges generation, leakage current reduction [29-41]. A thin and good quality SiO_2 or SiO_2-like is inevitable to prevent interfacial layer degradation. In this paper, we demonstrate different surface treatments by nitridation, rapid thermal oxidation (RTO), and dipped in the ozone water.

3.2 Experiment

First, 6-inch P-type Si wafers were cleaned by RCA clean and 50:1 HF dipped last. The 350Å pad oxide were formation at 950°C in the dry oxide furnace. Due to large stress between Si substrate and Si_3N_4, the pad oxide must be deposited to release stress and reduce damage. Then 1500Å thickness of Si_3N_4 was deposited on the pad oxide at 780°C in the nitride furnace. The photoresist was coating by track system and lithography and patterning by I-line stepper. Si_3N_4 and pad oxide were etched by Reaction Ion Etching and PR was stripped by ozone asher and H_2SO_4. The 5500Å field oxide was grown at 980°C in the wet oxide furnace and then **LOCOS formation.** The wafers were dipped in 7:1 BOE for 15 seconds and removed Si_3N_4. The sacrificial oxide was grown and striped and repeated itself.

These wafers were cleaned by RCA clean and HF dipped last. These samples were divided into 2 groups. One group was without Post Deposition Annealing (PDA) after Al_2O_3 deposition, the other was with PDA process after Al_2O_3 deposition. There were four different surface treatment conditions prior Al_2O_3 dielectric deposition. The four conditions were showed as below: 1. **w/o** treatment: Si substrate surface was without treatment before Al_2O_3 deposition. 2. **nitridation** treatment: the NH_3 treatment is performed in high temperature nitride furnace at 800°C for 1 hour. 3. **RTO** treatment: thin oxide was grown by the rapid thermal oxidation system at 800°C for 30 seconds. 4. **Ozone** treatment: the ultra-thin oxide formation using ozone water treatment at 2ppm for 5 minutes at room temperature.

After surface treatment, the 50Å or 80Å Al2O3 film was deposited by MOCVD, then with or without PDA process were performed at 900°C for 30 seconds in N_2 (5 slcm) ambient. Aluminum or TiN was deposited as gate electrode by thermal evaporation and physical vapor deposition, respectively. The PR coating and lithography were performed. Metal and aluminum oxide were etching by metal etcher and then MIS capacitors had been formed. Fig. 3-1 and Fig. 3-2 illustrates the MIS capacitor fabrication process flow and structure, respectively.

3.3 Results and discussions

3.3.1 50A° Al_2O_3 with Al gate electrode

Fig. 3-3 shows the comparison of C-V curves of the samples without and with PDA process at 900°C for 30 seconds in N_2 ambient. We can observe that C-V curves of samples without PDA process rose in the inversion area due to a lot of minority carriers which was induced by Si substrate defects or fabrication processes. From the C-V curves of samples with PDA process, the PDA process can eliminate the phenomenon. Fig. 3-4 shows the leakage current density comparison of samples without and with PDA process. In the PDA samples, it is evident that samples with various surface treatments including nitridation, RTO, and ozone can effectively reduce gate oxide leakage current. Fig. 3-5 illustrates Weibull plots for effective oxide thickness (EOT). We found that samples with PDA process can reduce effective oxide thickness. The uniformity of ozone water treatment samples seemed to be poor. The cause of poor uniformity is that the instrument of ozone water generation was stood in class 10k area which was unsuited to grow the gate oxide due to dirty environment. As ultra-thin oxide grown by ozone water treatment finished, we used nitrogen gun to purge water on the wafer. There were many small particles dropped on the wafer due to static electricity and the gate oxide quality of ozone water treatment became very poor. According to a series of ozone oxide growth experiments, we do not think that the uniformity of ozone oxide is poor.

Fig. 3-6 shows the Weibull plots of effective dielectric constant. After PDA process, the EOT of samples with surface treatments were improved than samples without treatment. According to recently studies, local dielectric crystallization result in effective dielectric constant enhanced. Fig. 3-7 shows Weibull plots for leakage current density at V_G-V_{FB}=-1V. The samples with nitridation and RTO treatments demonstrated lower leakage current due to the Si-N and Si-O bonds formation. The bonding strength comparisons as below: Si-O bond is 8.42 eV. Si-N bond is 4.75 eV. Si-Si bond is 3.38 eV. Si-H bond is 3.18 eV. We understood that bonding strength of Si-N and Si-O bonds are so stronger that the leakage current was lower. The leakage current of samples without surface treatment is large due to the poor interfacial layer characteristic. We knew that there were many interface states in the Si and high-k materials interface as high-k materials directly contact Si substrate. It is important that surface treatment is necessary process for utilization of high-k materials. The leakage current of all samples with PDA process is higher than without PDA process whether surface treatment or not. This reason is due to local dielectric crystallization and leakage current passed along the grain boundary easily. After PDA process, the leakage current of samples without surface treatment increased more than one order.

Fig. 3-8 illustrates the Weibull plots for time depend dielectric breakdown. The samples with nitridation treatment show better quality of time depend dielectric breakdown. Nitridation treatment induced many interface states, but surface nitridation may effectively reduce the concentration of oxygen vacancies and suppress oxygen diffusion. Although the Si-O bonds of samples with RTO treatment are stronger, but the density of RTO oxide is not dense. The oxygen molecule may pass through dielectric during dielectric deposition. The energy of oxygen molecule is not high due to lower temperature, so many dangling bonds may be induced. Because of dirty surface of samples with ozone water treatment, the quality is poor than nitridation and RTO treatments. The time depend dielectric breakdown of samples with PDA process can be improved effectively whether the surface treatment or not. Fig. 3-9 shows that constant voltage stress at V_G=-3.5V induced flatband voltage shift. The samples with surface treatment could improve the characteristics of flatband voltage shift whether PDA process or not. The samples without treatment showed that there are about 0.3~0.4V voltage shift before PDA process. It is evident that PDA process can reduce voltage shift phenomenon. Fig. 3-10 illustrates hysteresis curve for samples with and w/o surface treatments. We can find that PDA process can reduce effectively hysteresis phenomenon.

3.3.2 80A° Al_2O_3 with TiN gate electrode

In this study, split conditions of this experiment are listed as below. According to above experiment, the PDA process can improve high-k film quality. The samples are divided into two groups: PDA at 700°C and PDA at 900°C. Each group divided into three surface treatments: as-deposited, nitridation and ozone water treatment. The samples with ozone water treatment were dried by spin dry equipment.

Fig. 3-11 illustrates leakage current density versus electric field for samples with PDA 700°C and PDA 900°C. In the PDA 700°C samples, the leakage current of ozone water treatment demonstrated lowest leakage current. After PDA 900°C process, the leakage current of all samples was increased substantially. It was evident that the ozone treatment sample possessed the characteristic of lowest leakage current. Fig. 3-12 shows leakage current density comparison at 4MV/cm. We can find that sample with ozone treatment suppressed effectively leakage current both PDA 700˚C and 900 ˚C process.

Fig. 3-13 shows the normalize capacitance versus gate bias with PDA 700˚C and 900˚C process. From the C-V curve, the samples with ozone water treatment demonstrated the less interface states than without treatment and nitridation treatment after PDA 700˚C process. The interface states could reduce effectively by PDA 900˚C process. the inversion area of the ozone sample with PDA 900˚C rose due to a lot minority carriers. This was induced by silicon substrate defects. Fig. 3-14 (a)(b)(c) shows the capacitance versus gate voltage curve of various surface treatments with PDA 700˚C and PDA 900˚C, respectively. The capacitance value could increase with PDA 900˚C process due to higher temperature induced local film crystallization. Fig. 3-15 illustrates breakdown characteristic for samples with PDA 700˚C and PDA 900˚C. The ozone treatment can improve breakdown property. The samples with PDA 900˚C process possessed better breakdown characteristic than samples with PDA 700˚C process. Fig. 3-16 illustrates Weibull plots of effective dielectric constant for various surface treatments. Fig. 3-17 illustrates Weibull plot of effective oxide thickness. Fig.3-18 shows the hysteresis characteristic of all samples. The hysteresis can be reduced by PDA 900˚C process.

3.3.3 Samples with ozone water treatment followed by RTO or Nitridation

First, all samples had been treated by ozone water treatment to grow a thin oxide. Then the samples were divided into two groups. One was RTO 800°C for 30 seconds, and the other was RTO 800°C for 30 second followed by NH3 treatment for 1 hour.

Fig. 3-19 shows leakage current density versus electric field for various ozone treatments. The ozone treatment followed by RTO and nitridation possessed the lower leakage current in PDA 700°C process. In PDA 900°C process, just ozone treatment possessed lower leakage current. Fig. 3-20 shows the C-V curve for various ozone treatments. Fig. 3-21 illustrates the C/Cox curve for ozone treatments with PDA 700°C and PDA 900°C. The samples with PDA 900°C process show higher capacitance value and fewer interfaces states. Fig. 3-22 illustrates breakdown characteristic for various ozone treatments with PDA 700°C and PDA 900°C. The samples with ozone water treatment followed by RTO demonstrate higher breakdown electric field due to thicker interfacial layer. Because nitridation may induce more interface states, ozone water treatment with RTO followed by nitridation process shows smaller breakdown electric field than ozone water treatment followed by RTO process. Fig. 3-23 shows that Weibull plots for effective dielectric value of various ozone treatments with PDA 700°C and PDA 900°C. The PDA 900°C process shows higher effective k value.

3.4 Summary

In this chapter, various surface treatments such as nitridation, RTO, ozone and various temperature of PDA process are present. It is evidence that the interfacial layer grown by ozone water can effectively reduce leakage current and PDA at 900°C can improve capacitance value. From this study, nitridation treatment also reduced leakage current, but the interfaces states might be increased. We demonstrate that ozone oxide and PDA 900°C are the best choice.