PROCESS CONTROL OF RAPID THERMAL N₂O-ANNEALED THIN GATE OXIDES

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Abstract—The effects of rapid thermal post-oxidation N₂O anneal on conventional thermal oxides are studied in this work. The initial characteristics of oxide, including time-zero dielectric breakdown (TZDB), flat-band voltage (V_{FB}), and midgap interface trap density (D_{itm}), show dependence on the N₂O annealing time and temperature. The degradation of performances after ⁶⁰Co γ -ray irradiation is limited by the presence of N₂O anneal and also depends on the N₂O annealing conditions. It is believed that the incorporation of nitrogen atoms into the SiO₂/Si interface is responsible for the improved quality of the oxide.

1. INTRODUCTION

Nitridation of the conventional thermal oxide has received much attention for its ability to improve the quality of oxide. Many advantages of nitrided gate oxides, including physical characteristics and electrical properties, were proposed. For example, the thermal nitrided oxides are resistant to the penetration of dopant and Al atoms[1], have a high dielectric strength, and are resistant to the damages induced by radiation[2,3]. There are many methods, such as implantation of nitrogen atoms[4], NH₃ nitridation[5], and N₂O anneal[6], etc., by which nitrogen atoms can be incorporated into SiO₂/Si interface. Among these methods, the N₂O anneal exhibits attractive properties, such as its greater convenience in comparison with implantation and no introduction of hydrogen-related species due to NH₃ nitridation[7]. Generally speaking, the incorporation of nitrogen atoms can release the interfacial strain and improve the quality of oxide. However, it has also been reported that high-temperature or long-time N₂O anneal will degrade the oxide quality[8]. Therefore, there may be an optimum condition of N₂O treatment. In this work, an effort is made to find out the dependency of oxide quality on the N₂O annealing conditions.

It is known that both the furnace and the rapid thermal system can be employed to carry out N₂O annealing. However, the necessary long-time annealing process of the traditional furnace will waste a large amount of N₂O gas and also result in the redistribution of impurity[5]. On the contrary, the thermal budget is more easily controlled for the rapid thermal system than for the conventional furnace. Hence, the rapid thermal system is used for the preparation of N₂O annealing processes in this work.

2. EXPERIMENTAL

The MOS capacitors used in this study were fabricated on *p*-type (100) silicon wafers with resistivity between 5 and 10 Ω -cm. After standard RCA cleaning, 20 samples were firstly dry-oxidized in a conventional furnace at 980°C for 12 min and immediately followed by post oxidation annealing (POA) in pure nitrogen ambient at the same temperature for 10 min. At this moment, oxide thicknesses ranging from 86 to 96 Å were obtained. Then, samples were N₂O-annealed by the rapid thermal system in a 1 atm. ambient with various annealing conditions.

Four different annealing temperatures (900, 950, 1000, and 1050°C) and five distinct processing times (10, 30, 60, 120, and 200 s) were chosen to be the N₂O annealing conditions. In addition, another three samples with different treatments were prepared for comparison. One of them experienced dry oxidation in a conventional furnace at 980°C for 15 min with no following rapid thermal annealing and is denoted by FO. The other two were firstly oxidized by the rapid thermal system at 950°C in O₂-filled ambient for 80 s and in N₂O-filled ambient for 100 s, respectively. After oxidation, both samples were N₂O-annealed in the rapid thermal system at 950°C for 120 s and these two samples are denoted by RON and RNN, respectively. Table I lists variations in final oxide thicknesses and oxide thickness increase due to N₂O anneal for various N₂O conditions. The initial oxide thicknesses before N₂O anneal range from 86 to 96 Å.

Aluminium films were subsequently deposited on all samples and photolithography was used to pattern the metal gate. After back surfaces of samples were coated with evaporated aluminum films to serve as substrate contacts, the preparation of MOS capacitors with various gate oxides was finished. Each sample

Table 1. The variations in total oxide thickness (d_{ox}) after N_2O annealing and in oxide thickness increase (Δd_{ox}) due to N_2O annealing for various N_2O conditions

t_N	T_N			
	900	950	1000	1050
	Total $d_{ox}/\Delta d_{ox}$ due to N_2O annealing			
10	94/8	99/7	102/10	109/13
30	96/8	101/11	111/19	117/26
60	102/12	111/20	117/25	130/36
120	107/15	117/29	133/37	149/56
200	112/23	130/39	163/67	179/91

Furnace oxidation 980°C, 15 min 114/— (FO).

Rapid thermal 950°C O_2 80 s + N_2O 120 s 107/22 (RON).

Rapid thermal 950°C N_2O 100 s + N_2O 120 s 89/29 (RNN).

was cut into two pieces, and one of them was treated by post-metallization-annealing (PMA) at 400°C for 20 min in a pure nitrogen ambient while the other one received no further treatment. The former, with PMA treatment, was used for the measurement of $C-V$ characteristics and the latter was employed for the measurement of oxide breakdown field. The flat-band voltage V_{FB} and midgap interface trap density D_{itm} are calculated from high-low frequency $C-V$ curves. The irradiation is performed by ^{60}Co γ -rays with a total dose of 1 Mrad(SiO_2) and the devices were unbiased during irradiation in this work.

3. RESULTS AND DISCUSSION

3.1. Initial characteristics

Figure 1(a) which is drawn according to the data given in Table 1 shows the variation in oxide thick-

ness increase Δd_{ox} vs N_2O annealing time (t_N), and meanwhile, Fig. 1(b) presents the same characteristics vs N_2O annealing time (t_N). It can be found that as T_N goes higher or t_N becomes longer, the oxide thickness increases independently. At least, when T_N is lower than 1050°C and t_N is shorter than 200 s, no self-limited phenomenon that was reported by some researchers[9,10] can be observed in this work.

Figure 2(a) shows the average oxide breakdown field (E_{BD}) of all samples vs T_N . In every sample, 20 wide-distributed MOS-Cs, each with an area of $1.767 \times 10^{-4} \text{ cm}^2$, were measured, and the points with the highest and lowest values were excluded to obtain the average E_{BD} . All samples prepared by furnace oxidation and subsequent N_2O anneal have superior breakdown characteristics to the sample FO. Generally speaking, the average E_{BD} decreases as T_N increases and this means that as high as 1050°C N_2O anneal worsens the oxide breakdown behavior. Furthermore, Fig. 2(b) shows the relationship between E_{BD} and t_N , and it can be found that the optimum t_N decreases while T_N increases except the 1050°C condition.

The RON sample shows worse breakdown behavior than all other samples while the RNN sample exhibits better but still below average breakdown characteristics. From the observation in this work, both long-time and high-temperature N_2O annealing will make the breakdown behavior worse. Nevertheless, it seems that there is not sufficient nitrogen atoms incorporated into the SiO_2/Si interface to effectively

Fig. 1. The variation in oxide thickness increase Δd_{ox} vs N_2O annealing: (a) temperature T_N and (b) time t_N .

Fig. 2. The relationship between average oxide breakdown field E_{BD} and N_2O annealing: (a) temperature T_N and (b) time t_N .

Fig. 3. The Weibull plots of E_{BD} for samples: (a) annealed at 950°C for various annealing times and (b) annealed for 120 s at various annealing temperatures.

improve the quality of oxide for the samples with short N₂O annealing time, e.g. 10 s, while a longer annealing time can do better. Among all samples, the 900°C, 120 s annealing case gives the highest average oxide breakdown field.

Figure 3(a) portrays the Weibull plots of E_{BD} for the samples annealed at 950°C with various annealing times and Fig. 3(b) gives similar characteristics of the samples annealed for 120 s at different T_N . From observation, it can be found that the 30 s annealing sample exhibits very sharp distribution in E_{BD} , i.e. about 14 MV/cm. In addition, the long-time annealed oxide, e.g. 200 s, also gives sharp distribution but much lower E_{BD} . On the other hand, the 10 s annealed sample shows even higher but widely-distributed E_{BD} because of nonuniformity which may be due to not enough annealing time.

The comparison of initial oxide quality can also be observed from the variation in initial flat-band voltage (V_{FB}) and midgap interface trap density (D_{itm}) vs T_N which are shown in Figs 4(a) and 5(a), respectively. As T_N goes higher, V_{FB} will become more negative and D_{itm} will increase. This represents the incorporation of more nitrogen atoms due to higher annealing temperature. The nitrogen atoms incorporated in the gate oxides can replace the oxygen atoms and introduce a large amount of defects in the oxide bulk and at the SiO₂/Si interface. However, the short T_N sample gives less negative V_{FB} and smaller

Fig. 4. Variations in flat-band voltage V_{FB} vs N₂O annealing: (a) temperature T_N and (b) time t_N .

Fig. 5. Variations in midgap interface trap density D_{itm} vs N₂O annealing: (a) temperature T_N and (b) time t_N .

D_{itm} than the high t_N sample which can be observed from Figs 4(b) and 5(b), but the phenomenon seems not so obvious.

The oxide, FO, exhibits less negative V_{FB} and smaller D_{itm} than the RON and RNN which were prepared just by rapid thermal processing. However, when it is compared with samples prepared by furnace oxidation then rapid thermal annealing, the FO sample exhibits modest values for both V_{FB} and D_{itm} . It can be told that the appropriate choices of the rapid thermal N_2O annealing temperature and time do improve the initial oxide quality through the incorporation of nitrogen atoms. Nevertheless, long-time and high-temperature N_2O annealing will not benefit, but will damage the initial oxide quality. It is interesting that the V_{FB} of the RNN oxide is less negative than that of the RON oxide, although the former gives larger D_{itm} than the latter. It is known that both bulk oxide charges and interface traps can affect the flat-band voltage. That is to say, if the oxide is N_2O -grown at the beginning, more interface traps will be introduced which is contrary to the increased bulk oxide charges introduced by rapid thermal O_2 oxidation.

3.2. Radiation effects

Figure 6(a) illustrates the high-low frequency $C-V$ curves of the oxide, which was prepared by furnace oxidation and rapid thermal N_2O annealing at 950°C

Fig. 6. The high-low frequency $C-V$ curves for oxides prepared by: (a) furnace oxidation and rapid thermal N_2O anneal at 950°C for 120 s, and (b) only furnace oxidation, before and after 1 Mrad(SiO_2) ^{60}Co irradiation.

Fig. 7. Variations in radiation induced flat-band voltage shift ΔV_{FB} vs N_2O annealing: (a) temperature T_N and (b) time t_N .

Fig. 8. Variations in radiation induced midgap interface trap density shift ΔD_{itm} vs N_2O annealing: (a) temperature T_N and (b) time t_N .

for 120 s, before and after irradiation. At the same time, the $C-V$ curves for the oxide without N₂O annealing, i.e. FO, are also provided as in Fig. 6(b) for comparison. It is obvious that irradiation results in larger ΔV_{FB} and ΔD_{itm} for the oxide without N₂O annealing than with N₂O annealing.

Figures 7(a) and 8(a) show the radiation-induced flat-band voltage shift (ΔV_{FB}) and midgap interface trap density shift (ΔD_{itm}) vs T_N , respectively. From these figures, it can be observed that the oxide without N₂O annealing has the largest ΔV_{FB} and ΔD_{itm} . This shows that the incorporation of nitrogen atoms by rapid thermal N₂O annealing does improve the radiation hardness of oxide.

Generally speaking, as T_N increases, both ΔV_{FB} and ΔD_{itm} decrease at first, and then increase if T_N increases continuously. A similar behavior can be observed as t_N increases, which is shown in Figs 7(b) and 8(b). The samples with 950°C N₂O annealing give less changes in characteristics than those with other processing temperatures. At the same time, the oxides treated by 60 s N₂O annealing seem to be more radiation hard than others, although the 950°C, 60 s N₂O annealed oxide is not the most radiation hard among all samples. The samples RON and RNN exhibit good behavior after irradiation and do not show many differences because they both received N₂O treatment.

4. CONCLUSION

It is noted that samples having good initial properties may not have good hardness to radiation. This is mainly due to the different requirements of interfacial stress or bond strength at the SiO₂/Si interface between these characteristics. Therefore, the radiation

hardness behavior, as shown in Figs 7 and 8, differs from the initial properties, as shown in Figs 4 and 5. From the observations in this work, it is seen that proper choices of processing temperature and annealing time are necessary for reliable N₂O-annealed gate oxides. The high-temperature induced viscous flow at the SiO₂/Si interface, the relaxation of interfacial strain, the incorporation of nitrogen atoms, etc., are factors determining the oxide quality. It is proved that rapid thermal N₂O annealing does benefit radiation hardness of devices. However, the choices of annealing time and temperature play an important role at this moment. These are important to the study of rapid thermal thin gate oxides.

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