High Quality CVD/Thermal Stacked Gate Oxide Films with Hydrogen-Free CVD SiO₂ Formed in the SiCl₄-N₂O System

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We have developed and evaluated CVD SiO₂ films formed in a hydrogen-free system. That is, SiCl₄ (tetrachlorosilane; TCS) and N₂O have been employed as LPCVD source gases. It was found that the hot-carrier degradation, the constant current TDDB and the charge-trapping characteristics of CVD SiO₂ films prepared from TCS and N₂O (TCS-SiO₂) are superior to those of conventional CVD SiO₂ films formed from SiH₂Cl₂ and N₂O. We have concluded that TCS-SiO₂ is appropriate for CVD/thermal stacked oxide films due to its lower electron trap density and due to its promise of higher reliability of gate oxide films.

1. INTRODUCTION

CVD/thermal stacked oxide films have received much attention as candidates for thin gate dielectrics in quarter micron devices 1,2). These stacked oxide films show promise for the suppression of the thinning effect at isolation edges³). CVD oxide films prepared from SiH₂Cl₂ (DCS) and N₂O have been used conventionally. However, these films have a higher electron trap density attributed to the incorporation of hydrogen-containing species, i.e., Si-H and Si-OH bonds are generated in LPCVD reactions. Therefore, as an alternative to a conventional CVD oxide film, we propose the CVD SiO₂ film formed from a non-hydrogencontaining Si source (SiCl₄; TCS) and N₂O. In this paper, we present the electrical characteristics of a CVD/thermal stacked oxide film with CVD SiO2 prepared from TCS and N_2O (TCS-SiO₂) and compare this film to both a dry oxide film and a CVD/thermal stacked oxide film with a conventional CVD SiO₂.

2. EXPERIMENTAL

We have investigated two types of CVD SiO₂ films (TCS-SiO₂ and conventional) and a thermal oxide film. MOS capacitors with n⁺ poly-Si gates and n-channel MOSFETs (NMOSFETs) with Lightly Doped Drain (LDD) structure were fabricated using LOCOS isolation. All wafers received a 450°C post anneal in a hydrogen ambient. Conventional CVD SiO₂ films were prepared with DCS and N₂O (DCS-SiO₂) preceded by thermal oxidation. The dry oxide film was grown in a dry O₂ ambient. The structures of the CVD/thermal stacked gate oxide films with these two types of CVD SiO₂ employed in this study are illustrated in Fig. 1. The thickness of the gate oxide films were 5-6 nm.

3. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show Si_{2p} and O_{1s} x-ray photoelectron spectroscopy (XPS) spectra of the films prepared with TCS and N₂O and prove that SiO₂ films are really formed because the spectra are almost identical with those of thermal oxide films.

Table 1 compares the etching rate of a TCS-SiO₂ film and a DCS-SiO₂ film with a HF (HF:H₂O=1:200) solution. The etching rate of a TCS-SiO₂ film is reduced to half of that of a DCS-SiO₂ film. It suggests that a TCS-SiO₂ film is denser than a DCS-SiO₂ film.

Figure 3 represents the gate voltage shift of MOS capacitors under constant current injection. The electron injection was performed from the gate at the current density of 0.1 mA/cm². The large shift in the gate voltage caused by electron traps can be observed in the sample with a DCS-SiO₂ film. On the other hand, the TCS-SiO₂ film shows less electron trap generation as compared with the DCS-SiO₂ film, which may be due to the reduction of hydrogen-containing species.

A comparison of the C-V measurements of MOS capacitors using a TCS-SiO₂ film versus a dry oxide film was also carried out. Figure 4 compares the mid-gap voltage shift after a 25 mC/cm² electron injection from the gate. It was found that the TCS-SiO₂ film has a much smaller positive charge trap density as compared with the dry oxide film. This result is consistent with the fact that the gate voltage shift of a MOS capacitor with a TCS-SiO₂ film is slightly smaller than that with a dry oxide film as shown in Fig. 3.

TDDB characteristics of MOS capacitors under constant current stress are illustrated in Fig. 5(a) and 5(b), where the electron injection was performed from the substrate at the current density of 0.1 A/cm². The TCS-SiO₂ film has a larger charge to breakdown value at 50 % cumulative failure (50 % QBD) than the dry oxide film. The DCS-SiO₂ film has a smaller 50 % Q_{BD} as compared with the TCS-SiO₂ film. This is attributed to the larger electron trap density in the oxide films as mentioned earlier. Figure 6 shows a 50 % QBD in constant current TDDB measurements of MOS capacitors, where the electron injection was performed from the gate at the current density of 0.01 A/cm². The TCS-SiO₂ film has a larger 50 % Q_{BD} as compared with dry oxide film; moreover, the electron injection was performed from the substrate. These results show that the TCS-SiO₂ films have great potential as reliable gate oxide films.

Figures 7 and 8 show the hot carrier degradation for

NMOSFETs, presenting the degradation of drain current and the variation of charge-pumping current caused by DAHC (Drain Avalanche Hot Carrier) injection. The TCS-SiO₂ film and the dry oxide film exhibit slightly higher hotcarrier-degradation tolerance as compared with the DCS-SiO₂ film. The measurements of charge pumping current show that the interface state generation is reduced for both the TCS-SiO₂ film and the DCS-SiO₂ film. It may be due to the incorporation of a small amount of nitrogen at the SiO₂/Si interface. Therefore, the improvement in the hotcarrier reliability of the TCS-SiO₂ film can be explained by the reduction of electron trap density in the gate oxide film.

4. CONCLUSION

We have developed and evaluated CVD SiO₂ films formed in a hydrogen-free system. That is, TCS and N₂O have been employed as LPCVD source gases. It was found that the hot-carrier degradation, the constant current TDDB and the charge-trapping characteristics of TCS-SiO₂ films are superior to those of conventional CVD SiO₂ films formed from DCS and N₂O. Moreover, the TDDB characteristics of a TCS-SiO₂ film under both bias conditions are superior to those of a dry oxide film. We have concluded that TCS-SiO₂ is appropriate for CVD/thermal stacked oxide films due to its lower electron trap density and due to its promise of higher reliability of gate oxide films.

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Fig. 2 (a) Si_{2p} and (b) O_{1s} XPS spectra of the CVD oxide films prepared with TCS and N_2O .

Table 1 Etching rate of two types of CVD SiO₂ films.

DCS-SiO ₂	2.4 nm/min
TCS-SiO ₂	1.2 nm/min



Fig. 3 Gate voltage shift of MOS capacitors during constant current stressing of -0.1 mA/cm².



Fig. 4 Mid-gap voltage shift extracted from the C-V measurements after a 25 mC/cm² electron injection from the gate.



Fig. 5 (a) Weibull plots and (b) Q_{BD} at 50 % cumulative failure in constant current TDDB measurements. The electron injection was performed from the substrate at the current density of 0.1 A/cm².



Fig. 6 Q_{BD} at 50 % cumulative failure in constant current TDDB measurements. The electron injection was performed from the gate at the current density of 0.01 A/cm².



Fig. 7 Degradation of drain current for NMOSFETs (L=0.5 μ m, W=10 μ m) during the DAHC injection. The stress was applied at Vd=4.5V, Vg=V(I_{sub,max}) for 1000 sec.



Fig. 8 Variation of the charge pumping current for NMOSFETs (L=100 μ m, W=100 μ m) during the DAHC injection. The stress was applied at Vd=8V, Vg=V(I_{sub,max}) for 1000 sec.