Reduction of Leakage Current in Chemical-Vapor-Deposited Ta$_2$O$_5$ Thin Films by Furnace N$_2$O Annealing

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Abstract—In this brief, we present a post-deposition annealing technique that employs furnace annealing in N$_2$O (FN$_2$O) to reduce the leakage current of chemical-vapor-deposited tantalum penta-oxide (CVD Ta$_2$O$_5$) thin films. Compared with furnace annealing in O$_2$ (FO) and rapid thermal annealing in N$_2$O (RTN$_2$O), FN$_2$O annealing proved to have the lowest leakage current and the most reliable time-dependent dielectric breakdown (TDDB).

I. INTRODUCTION

In view of its inherently high dielectric constant (~25) and excellent step coverage, chemical-vapor-deposited tantalum penta-oxide (CVD Ta$_2$O$_5$) has been studied extensively for the storage dielectrics in high-density dynamic random access memories (DRAM’s) [1]–[3]. However, because of its poor film quality, the as-deposited film had been considered too leaky for DRAM applications. Various post-deposition annealing techniques have been proposed for improving the film quality and reducing the leakage current of CVD Ta$_2$O$_5$. e.g., plasma O$_2$ [4], [5], furnace dry-O$_2$ (FO) [6], [7], UV–O$_2$ and furnace dry-O$_2$ [8], [9], and rapid thermal O$_2$ (RTO) annealing [10], [11].

In recent years, due to its ability to incorporate nitrogen into the Si/SiO$_2$ interface, the use of N$_2$O as an oxidant or an annealing gas for gate dielectrics has attracted significant attention. As a result, in order to improve the reliability properties of MOS devices, the oxynitride gate dielectrics have been suggested as an alternative to conventional SiO$_2$. Both rapid thermal processing and conventional furnaces have been used to grow oxynitrides in N$_2$O [12], [13]. Since post-deposition thermal treatment by rapid thermal annealing in N$_2$O (RTN$_2$O) has shown demonstrated potential to improve the electrical properties of CVD Ta$_2$O$_5$ films [14], it is desirable to broaden its application using conventional furnaces for Ta$_2$O$_5$ dielectrics in DRAM storage capacitors.

In this brief, we report a new post-deposition annealing technique that employs furnace annealing in N$_2$O (FN$_2$O) to reduce the leakage current of as-deposited films.

II. EXPERIMENTAL

Thin Ta$_2$O$_5$ films (~16 nm) were deposited on phosphorus-doped poly-Si bottom electrodes by low-pressure chemical vapor deposition (LPCVD) at 450 °C and 80 Pa, using Ta(OC$_2$H$_5$)$_5$ and O$_2$. Prior to Ta$_2$O$_5$ deposition, the polysilicon surface was treated by rapid thermal nitridation (RTN) in NH$_3$ at 900 °C for 60 s to maximize film storage efficiency and improve the leakage current and reliability characteristics [9]. After deposition, Ta$_2$O$_5$ films were subjected to annealing in three different conditions. These include 1) FO at 800 °C for 30 min, 2) RTN$_2$O at 800 °C for 60 s, and 3) FN$_2$O at 800 °C for 30 min. Finally the TiN and aluminum top electrode was formed by reactive sputtering and subsequent patterning.

III. RESULTS AND DISCUSSION

Fig. 1 displays the leakage current characteristics of 16-nm thick Ta$_2$O$_5$ capacitors before and after annealing processes.

![Figure 1](image_url)

Fig. 1. Leakage current characteristics of 16-nm thick Ta$_2$O$_5$ capacitors before and after annealing processes.

The effective oxide electric field $E_{\text{eff}}$ was calculated by $V_d/T_{\text{off}}$, where $V_d$ is the applied voltage. The effective oxide thickness $T_{\text{eff}}$ was calculated from $C/V_dA$, where $C$ is the capacitance measured at 100 kHz, $\varepsilon_r$ is the permittivity in vacuum, $\varepsilon_r$ is the dielectric constant of SiO$_2$ (3.82), and $A$ is the area of the capacitor. The experimental results shown in Fig. 1 clearly indicate that FN$_2$O produces the lowest leakage current. A plausible mechanism for this reduction by FN$_2$O annealing can be attributed to the reactive atomic species (O) generated by the N$_2$O dissociation (N$_2$O -> N$_2$ + O$^*$) during the furnace thermal cycle [13]. N$_2$O generates an atomic oxygen much more effectively than molecular oxygen. In addition, atomic oxygen is a more effective oxidizing agent. The excited oxygen atoms 1) reduced the degree of imperfection caused by the deficiency of oxygen atoms adjacent to tantalum atoms (oxygen vacancy reduction), 2) reduced the defect density that is due to carbon and hydrogen contamination, and 3) grew interfacial oxide between Ta$_2$O$_5$ and underlying poly-Si. The remaining atomic oxygen recombines into molecular oxygen (O$_2$). High-temperature (800 °C) O$_2$ allows to reduce the defect density in a sufficient time (30 m versus 60 s). The foregoing explains why FN$_2$O annealing produces a lower leakage current and thicker interfacial SiO$_2$ layer than FO and RTN$_2$O annealing. The effective oxide thickness for each capacitor before annealing is 3.3 nm. The effective oxide thicknesses are 3.7, 3.7, and 4.0 nm after FO, RTN$_2$O, and FN$_2$O annealings, respectively. Fig. 2(a)–(c) shows the cross-sectional transmission electron microscopy (TEM) pictures of Ta$_2$O$_5$ film before, after FO annealing and after FN$_2$O annealing, respectively. Interlayers between the Ta$_2$O$_5$ films and the substrates can be seen in all three pictures. It was found that the thickness of the interfacial SiO$_2$...
Fig. 2. Cross-sectional TEM photographs of Ta$_2$O$_5$ (16-nm) films on Si substrate: (a) right after Ta$_2$O$_5$ deposition, (b) after FO annealing, and (c) after FN$_2$O annealing. Note that the SiO$_2$ layer grows between Ta$_2$O$_5$ and the Si substrate.

layers increases after FO and FN$_2$O annealing. Slightly thicker SiO$_2$ films are grown during FN$_2$O annealing, resulting in a capacitance reduction. FN$_2$O annealing is highly effective in suppressing leakage current at the slight cost of sacrificing the capacitance per unit area that arises from interfacial oxidation. Since 16-nm Ta$_2$O$_5$ films were used in this study, FN$_2$O annealing results in a relatively large effective SiO$_2$ thickness (4.0 nm). However, thinner Ta$_2$O$_5$ films (~10 nm) will reduce the effective oxide thickness for high-density DRAM’s with relatively little SiO$_2$ growth for the Ta$_2$O$_5$ thickness range larger than 5 nm [15]. FN$_2$O annealing is a single-step process that can simultaneously provide the excited atomic oxygen species and high-temperature annealing. Moreover, FN$_2$O annealing may be conducted in conventional oxidation furnaces in batch order, and is therefore perfectly suitable for commercial mass production, thereby reducing costs and increasing overall efficiency.

Fig. 3 illustrates the SIMS depth profiles of the as-deposited and annealed Ta$_2$O$_5$ films. Compared with the other two annealing techniques, the impurities of carbon and hydrogen existing in the as-deposited Ta$_2$O$_5$ film were significantly reduced by FN$_2$O annealing. In particular, the amount of carbon near the surface of the film is markedly reduced. The elimination of these impurities corresponds to the reduction in the leakage current of Ta$_2$O$_5$ films after the different annealing treatments as shown in Fig. 1. The O$^+$ generated in FN$_2$O annealing can effectively diffuse through Ta$_2$O$_5$ films as an oxidizing agent and decrease the carbon concentration associated with Ta–C bonds in the films. The unstable CO molecule formed during FN$_2$O annealing can easily escape from the Ta$_2$O$_5$ film [16]. As a result, the film is densified and the defect density is reduced.
biased at a 15 MV/cm effective oxide field. The plotted points of \( n \) and \( p \) respectively. The critical field is measured at a leakage current of \( 1 \mu \text{A/cm}^2 \). Capacitors with the top electrode positively and negatively biased, applied effective electric field under both gate biasing polarities.

Fig. 6. Lifetime extraction: time to 50% cumulative failure as a function of operation voltage yields dielectric lifetimes that are higher than the postulated reliability requirement (e.g., 10 y) for all capacitors. However, capacitors with \( \text{FN}_2\text{O} \) annealing demonstrate the best long-term reliability for DRAM applications.

IV. CONCLUSION

In conclusion, post-deposition \( \text{FN}_2\text{O} \) annealing is highly effective in suppressing leakage current of \( \text{Ta}_2\text{O}_5 \) capacitors. In comparison with FO and RTN\(_2\text{O} \) annealing, capacitors with \( \text{FN}_2\text{O} \) annealing possess higher critical field distributions as well as superior TDDB reliability. Moreover, furnace annealing is more attractive because of its process simplicity.

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REFERENCES