Briefs

Reduction of Leakage Current in Chemical-Vapor-Deposited Ta_2O_5 Thin Films by Furnace N_2O Annealing

S. C. Sun and T. F Chen

Abstract—**In this brief, we present a post-deposition annealing technique that employs furnace annealing in N_2O (FN_2O) to reduce the leakage current of chemical-vapor-deposited tantalum penta-oxide (CVD Ta_2O_5) thin films. Compared with furnace annealing in O_2 (FO) and rapid thermal annealing in N_2O (RTN_2O), FN_2O 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_2O_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_2O_5, e.g., plasma O_2 [4], [5], furnace dry-O_2 (FO) [6], [7], UV–O_3 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 in the Si/SiO_2 interface, the use of N_2O 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_2O [12], [13]. Since post-deposition thermal treatment by rapid thermal annealing in N_2O (RTN_2O) has shown demonstrated potential to improve the electrical properties of CVD Ta_2O_5 films [14], it is desirable to broaden its application using conventional furnaces for Ta_2O_5 dielectrics in DRAM storage capacitors.

In this brief, we report a new post-deposition annealing technique that employs furnace annealing in N_2O (FN_2O) to reduce the leakage current of as-deposited films.

II. EXPERIMENTAL

Thin Ta_2O_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 $Ta(OC_2H_5)_5$ and O_2. Prior to Ta_2O_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_2O_5 films were subjected to annealing in three different conditions. These include 1) FO at 800 °C for 30 min, 2) RTN_2O at 800 °C for 60 s, and 3) FN_2O at 800 °C for 30 min. Finally the TiN and aluminum top electrode was formed by reactive sputtering and subsequent patterning.

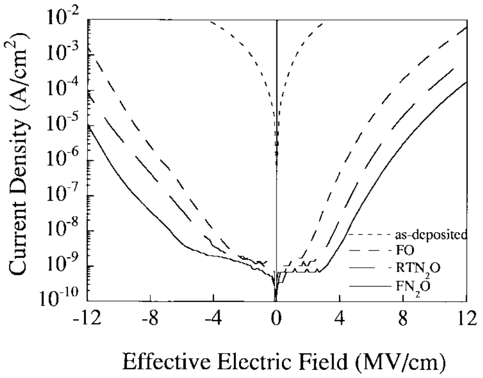

Fig. 1. Leakage current characteristics of 16-nm thick Ta_2O_5 capacitors before and after annealing processes.

III. RESULTS AND DISCUSSION

Fig. 1 displays the leakage current characteristics of Ta_2O_5 films before and after annealing treatments measured by the positive and the negative gate bias. The effective oxide electric field E_{eff} was calculated by V_g/T_{eff}, where V_g is the applied voltage. The effective oxide thickness T_{eff} was calculated from C–V characteristics and defined by $C/\varepsilon_o\varepsilon_s A$, where C is the capacitance measured at 100 kHz, ε_o is the permitivity in vacuum, ε_s 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_2O produces the lowest leakage current. A plausible mechanism for this reduction by FN_2O annealing can be attributed to the reactive atomic species (O^*) generated by the N_2O dissociation ($N_2O \rightarrow N_2 + O^*$) during the furnace thermal cycle [13]. N_2O 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_2O_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_2O annealing produces a lower leakage current and thicker interfacial SiO_2 layer than FO and RTN_2O 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_2O, and FN_2O annealings, respectively. Fig. 2(a)–(c) shows the cross-sectional transmission electron microscopy (TEM) pictures of Ta_2O_5 film before, after FO annealing and after FN_2O annealing, respectively. Interlayers between the Ta_2O_5 films and the substrates can be seen in all three pictures. It was found that the thickness of the interfacial SiO_2

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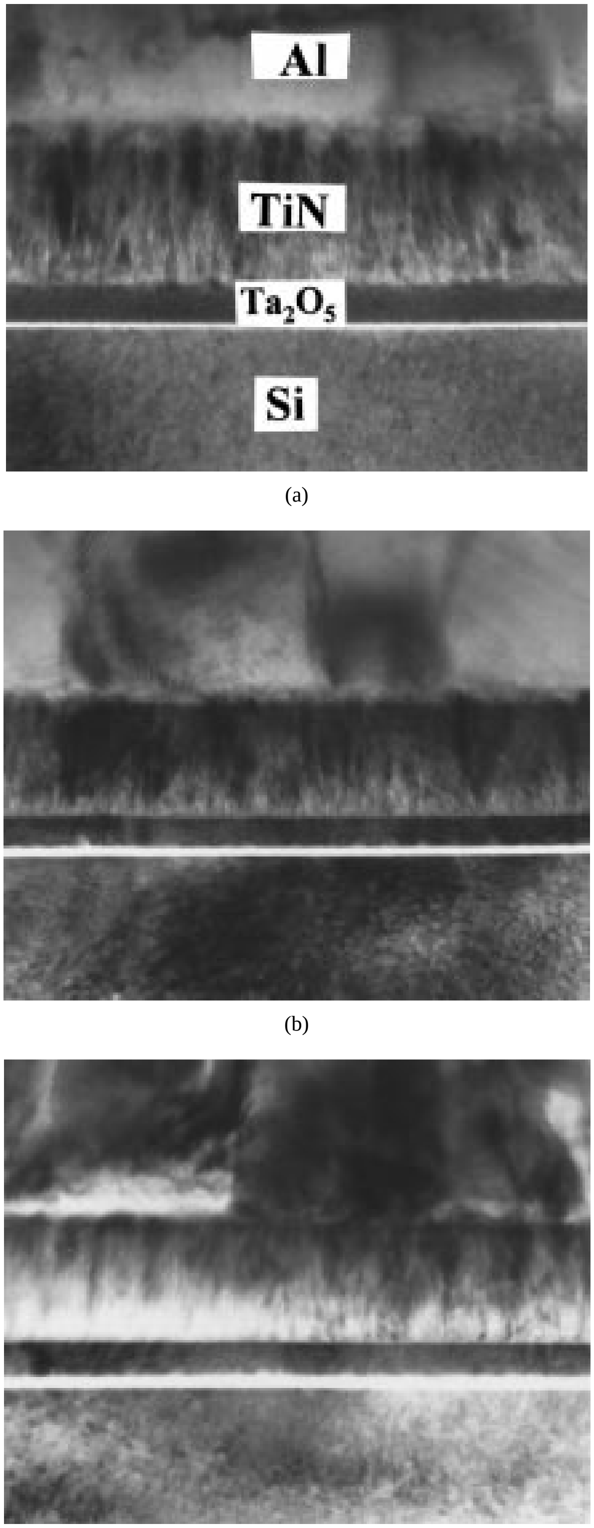

(a)

(b)

(c)

Fig. 2. Cross-sectional TEM photographs of Ta_2O_5 (16-nm) films on Si substrate: (a) right after Ta_2O_5 deposition, (b) after FO annealing, and (c) after FN_2O annealing. Note that the SiO_2 layer grows between Ta_2O_5 and the Si substrate.

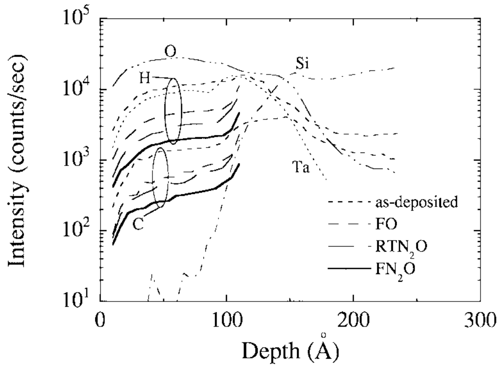

Fig. 3. SIMS depth profiles of as-deposited and annealed Ta_2O_5 films.

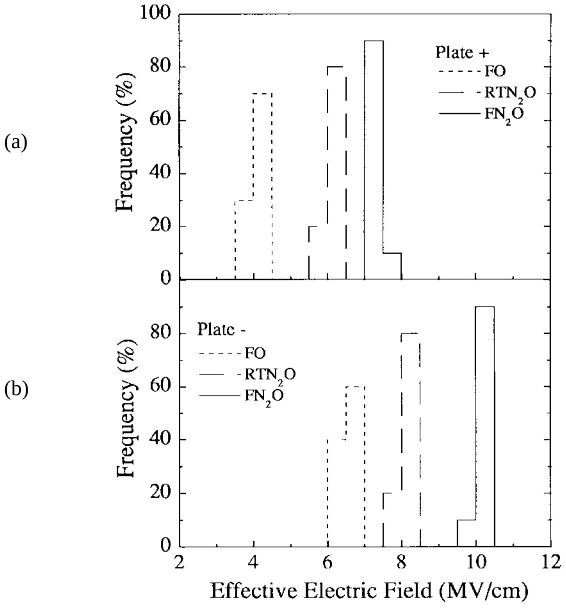

Fig. 4. The critical field histograms of Ta_2O_5 capacitors with top electrode biased at (a) positive and (b) negative voltages.

layers increases after FO and FN_2O annealing. Slightly thicker SiO_2 films are grown during FN_2O annealing, resulting in a capacitance reduction. FN_2O 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_2O_5 films were used in this study, FN_2O annealing results in a relatively large effective SiO_2 thickness (4.0 nm). However, thinner Ta_2O_5 films ($\sim$10 nm) will reduce the effective oxide thickness for high-density DRAM's with relatively little SiO_2 growth for the Ta_2O_5 thickness range larger than 5 nm [15]. FN_2O annealing is a *single-step* process that can simultaneously provide the excited atomic oxygen species and high-temperature annealing. Moreover, FN_2O 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_2O_5 films. Compared with the other two annealing techniques, the impurities of carbon and hydrogen existing in the as-deposited Ta_2O_5 film were significantly reduced by FN_2O 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_2O_5 films after the different annealing treatments as shown in Fig. 1. The O^* generated in FN_2O annealing can effectively diffuse through Ta_2O_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_2O annealing can easily escape from the Ta_2O_5 film [16]. As a result, the film is densified and the defect density is reduced.

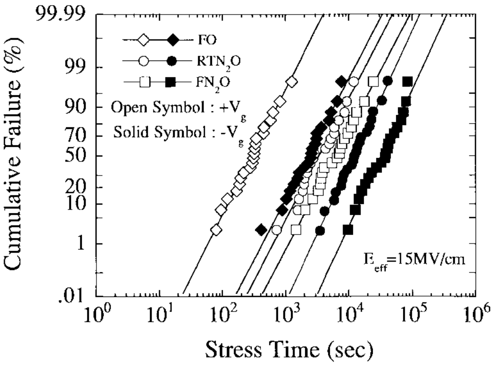

Fig. 5. TDDB stress time dependence of cumulative failure for Ta_2O_5 capacitors under both gate biasing polarities.

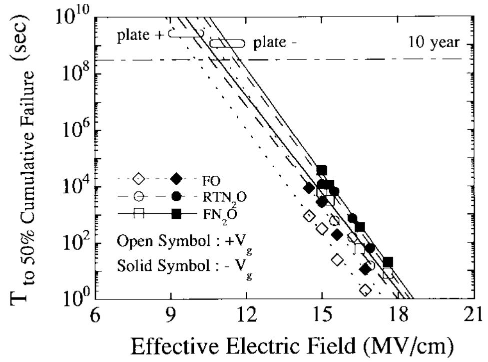

Fig. 6. Lifetime extraction: time to 50% cumulative failure as a function of applied effective electric field under both gate biasing polarities.

Fig. 4(a) and (b) illustrates the critical field histograms of Ta_2O_5 capacitors with the top electrode positively and negatively biased, respectively. The critical field is measured at a leakage current of 1 μA/cm^2. The capacitor area is 1.21×10^{-2} cm^2. FN_2O annealing possesses a higher critical field distribution compared with the other two annealing treatments. Those results indicate that FN_2O annealing effectively lowers the defect density arising from weak spots and hydrocarbon contamination, leading to an improvement in the electrical properties of Ta_2O_5 films. In addition, the dependence of the critical field on the bias polarity is clearly observed. This difference in critical voltage corresponds to the work function difference between the top electrode of TiN and the bottom electrode of n^+ poly-Si (the work function of TiN is 4.95 eV and that of n^+ poly-Si is 4.1 eV) [5], [17], [18].

The time-dependent dielectric breakdown (TDDB) stress time dependence of cumulative failure of Ta_2O_5 capacitors for three different annealing treatments is shown in Fig. 5. The capacitor area is 1.44×10^{-4} cm^2. The stress conditions are positive or negative biased at a 15 MV/cm effective oxide field. The plotted points follow straight lines, and random failure modes are not observed. This shows that Ta_2O_5 films after annealing are of high quality and of good uniformity. The TDDB stress time of 50% cumulative failure for FN_2O capacitors is about three and 15 times longer than that of RTN_2O and FO capacitors. Fig. 6 demonstrates the dependence of TDDB lifetime on the electric field under both stress polarities for annealed Ta_2O_5 films. The FO annealed film reveals the shortest lifetime to breakdown, the RTN_2O annealed film displays intermediate reliability characteristics, and the FN_2O annealed film has the longest breakdown time. The extrapolation of our data to operation voltage yields dielectric lifetimes that are higher than the postulated reliability requirement (e.g., 10 y) for all capacitors. However, capacitors with FN_2O annealing demonstrate the best long-term reliability for DRAM applications.

IV. CONCLUSION

In conclusion, post-deposition FN_2O annealing is highly effective in suppressing leakage current of Ta_2O_5 capacitors. In comparison with FO and RTN_2O annealing, capacitors with FN_2O 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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