Leakage Current Reduction in Chemical-Vapor-Deposited Ta₂O₅ Films by Rapid Thermal Annealing in N₂O

S. C. Sun, Member, IEEE, and T. F. Chen

Abstract— This study aims to improve the electrical characteristics and reliability of low-pressure chemical vapor deposited (LPCVD) Ta_2O_5 films by developing a new post-deposition single-step annealing technique. Experimental results indicate that excited oxygen atoms generated by N_2O decomposition can effectively repair the oxygen vacancies in the as-deposited CVD Ta_2O_5 film, thereby resulting in a remarkable reduction of the film's leakage current. Two other post-deposition annealing conditions are compared: rapid thermal O_2 annealing and furnace $dry\text{-}O_2$ annealing. The comparison reveals that RTN_2O annealing has the lowest leakage current, superior thermal stability of electrical characteristics and the best time-dependent dielectric breakdown (TDDB) reliability.

I. INTRODUCTION

IGHLY integrated DRAM's require an extremely thin dielectric film for these dielectric film for the dielectric film film for the dielectric film for the dielectric film for the dielectric film for the dielectric film film for the dielectric film for the dielectric film for the dielectric film film for the dielectric dielectric film for three-dimensional (3-D) stacked or trenched capacitors [1]-[2]. To satisfy 256 Mb or 1 Gb DRAM requirements, considerably higher capacitance values are necessary to keep the cells structures simple and manufacturable. For this purpose, CVD Ta₂O₅ has been demonstrated to be a highly promising storage dielectric material for high-density DRAM applications [3]-[10] owing to its high dielectric constant and excellent step coverage [9]-[10]. The as-deposited CVD Ta₂O₅ capacitors exhibited an extensive leakage current [3]-[10]. Moreover, various postdeposition annealing techniques, e.g., plasma O₂ [4], UV-O₃ [5]-[6], furnace dry- O_2 (FO) [7]-[9], UV- O_3 and dry O_2 [5], and rapid thermal O₂ annealing (RTO) [11]-[12], have been proposed to reduce the leakage current and improve the quality of Ta₂O₅. During the thermal treatment in the oxygencontaining ambient, oxygen diffuses into the Ta₂O₅ films, leading to repair of oxygen vacancies, elimination of organic inclusions, and reduction of weak spots in the tantalum oxide films [5].

Our recent work presented preliminary results using a new fabrication technique for leakage current reduction of CVD Ta₂O₅ films [13]. The process involves a relatively simple and effective *single-step* thermal treatment of the as-deposited Ta₂O₅ films using rapid thermal annealing in N₂O (RTN₂O). In extending our previous work, this paper attempts to more thoroughly understand the effects of post-deposition RTN₂O

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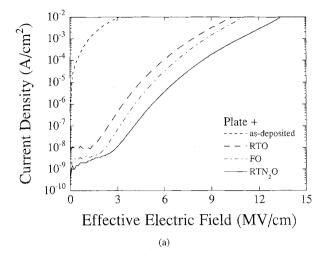
on the electrical properties and reliability of CVD ${\rm Ta_2O_5}$ deposited on NH₃-nitrided poly-Si substrates.

II. EXPERIMENTAL.

Planar capacitors with phosphorus-doped poly-Si bottom electrodes, 16-nm CVD Ta_2O_5 dielectric materials, and TiN top electrodes were fabricated on 100 mm n-type (100) silicon substrates. 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. The $Ta(OC_2H_5)_5$ source was vaporized at 110°C and then introduced into the reaction chamber by argon carrier gas at the same time in which oxygen gas was introduced. The deposition temperature was 450°C and the total gas pressure was maintained at 80 Pa. After deposition, each CVD Ta_2O_5 film was subjected to one of the following annealing processes: a) RTO at 800°C for 60 s; b) FO at 800°C for 30 min; and c) RTN $_2O$ at 800°C for 60 s. Finally, TiN and aluminum top electrode was formed by reactive sputtering and then patterned to form the capacitor's top plate.

III. RESULTS AND DISCUSSION

Fig. 1(a) and (b) present the typical results of the currentvoltage characteristics of Ta₂O₅ films before and after annealing treatments with the gate positively and negatively biased, respectively. The effective oxide electric field $E_{\rm eff}$ was calculated from C-V characteristics and defined by $CV_q/\varepsilon_0\varepsilon_sA$, where C is the capacitance measured at 100 kHz, V_g is the applied voltage, ε_0 is the permittivity in vacuum, ε_s is the dielectric constant of SiO₂ (3.82), and A is the area of the capacitors. The capacitors with the as-deposited films have a large leakage current, possibly due to the inferior film structure. Small difference between the leakage current of positive and negative polarities suggests that the conduction mechanism may be primarily due to the bulk-limited conduction. The leakage current was reduced by the RTO annealing. FO annealing was more effective in reducing the leakage current than RTO annealing. RTN2O annealing shows the lowest leakage current at the same operating voltage. The leakage current was significantly reduced to 10^{-8} A/cm² at $E_{\rm eff}=3$ MV/cm for a positively biased, RTN₂O annealed Ta_2O_5 films. On the other hand, leakage currents are 7×10^{-8} and 5×10^{-7} A/cm² for FO and RTO annealed samples. All annealed films show a polarity asymmetry of leakage current characteristics. The leakage current for a negative bias is smaller than a positive bias, the former having a value of



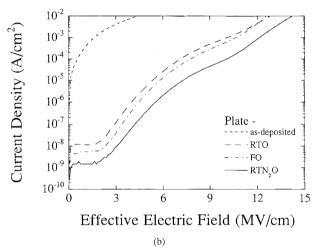


Fig. 1. Leakage current characteristics of 16-nm thick ${\rm Ta_2\,O_5}$ capacitors before and after annealing processes at (a) positive and (b) negative gate bias.

 9×10^{-9} , 4×10^{-8} , and 10^{-7} A/cm² at 3 MV/cm for RTN₂O, FO, and RTO annealed samples, respectively. This can be explained by the difference in the work function of n^+ poly-Si and TiN electrodes and by the composite dielectric structure (e.g. Ta_2O_5 stacked with Si_3N_4 or SiO_2) [3], [8]. In comparing the leakage current, it must be noted that the effective oxide thickness for each capacitor before annealing is 3.4 nm. The effective oxide thicknesses are 3.7 nm, 3.8 nm, and 3.8 nm after RTO, FO, and RTN₂O annealing, respectively.

A plausible mechanism for leakage current reduction by RTN₂O annealing can be attributed to the reactive atomic oxygen species (O^+) generated by the dissociation of N₂O gas at elevated temperature (N₂O \rightarrow N₂ + O⁺) during the rapid thermal process cycle [14]. These reactive oxygen species diffuse into Ta₂O₅ films and repair oxygen vacancies, thereby leading to a lower leakage current [5]. RTN₂O annealing is a *single-step* process capable of simultaneously providing the excited atomic oxygen species and high-temperature annealing. The excited oxygen atoms reduced the degree of imperfections caused by the deficiency of oxygen atoms adjacent to the tantalum atoms [15]. The remaining atomic oxygen

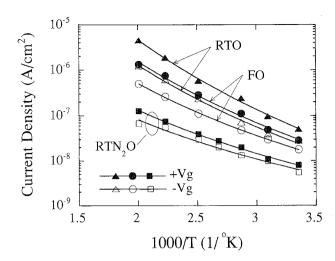


Fig. 2. Current density versus 1/T for capacitors with various annealing treatments.

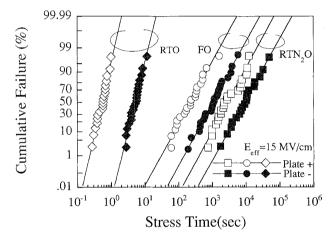


Fig. 3. TDDB stress time dependence of cumulative failure for ${\rm Ta_2O_5}$ capacitors under both gate biasing polarities.

recombines into molecular oxygen (O_2) . High-temperature $(800^{\circ}C)$ O_2 annealing reduced the defect density due to weak spots and carbon contamination [5]. On the other hand, FO annealing and RTO annealing rely on the diffusion of molecular oxygen (which is less reactive than the atomic oxygen) in repairing the oxygen vacancies of Ta_2O_5 films. Notably, an FO annealing time of 30 min is not as effective as a 60 s of RTN₂O in reducing leakage current. Furthermore, RTO annealing is even less effective than FO annealing owing to the insufficient time to allow oxygen molecules to reduce defects.

A previous investigation indicated that NO-nitridation is a more efficient method for incorporating nitrogen in the $\mathrm{Si/SiO_2}$ interface for gate dielectric formation than $\mathrm{N_2O}$ -nitridation [16]–[17]. In a separate work rapid thermal NO (RTNO) annealing was performed on as-deposited films [18]. Those results demonstrated that the RTNO annealing is less effective than RTN₂O annealing in reducing the leakage current. Therefore, incorporating nitrogen in the dielectric and piling up at the $\mathrm{Ta_2O_5/poly\text{-}Si}$ interface caused by the RTN₂O

annealing apparently play only a minor role in leakage current reduction. The RTNO experiment also supports our earlier postulate that the atomic oxygen species generated by the N_2O dissociation is primarily responsible for the leakage current reduction.

Fig. 2 compares the temperature dependence of the leakage current characteristics for ${\rm Ta_2O_5}$ capacitors under both gate biasing polarities at $|V_g|=1$ V over the temperature range from 25°C to 225°C. The temperature stability of the low field leakage for RTN₂O annealed ${\rm Ta_2O_5}$ film is superior to films annealed by either FO or RTO.

Fig. 3 shows the TDDB stress time dependence of cumulative failure for annealed Ta₂O₅ capacitors. The capacitor area is 1.44×10^{-4} cm². The stress conditions are positive or negative biases at a 15 MV/cm effective oxide field. The plotted points follow straight lines, and random failure modes are not observed, indicating that the CVD Ta₂O₅ capacitors are of high quality and good uniformity. The RTO sample always has the shortest breakdown time and the FO sample displays intermediate reliability characteristics. The TDDB stress time of 50% cumulative failure for RTN₂O capacitors is about 10, and 5000 times longer than that of FO and RTO capacitors. Also, TDDB under different electric fields was investigated. Capacitors with RTN₂O annealing show a longer lifetime than the others. The extrapolated long-term lifetime indicates that RTN₂O capacitors can survive 10 years at a stress field of 8 MV/cm. Therefore, we believe that capacitors with 800°C, 60 s RTN₂O have the best long-term reliability for actual DRAM applications.

IV. CONCLUSION

In conclusion, using RTN $_2$ O post-deposition treatment of CVD Ta $_2$ O $_5$ films results in capacitors with reduced leakage current, superior TDDB reliability, and excellent temperature stability of electrical characteristics as compared with rapid thermal O $_2$ annealing and furnace dry-O $_2$ annealing. This technique is a highly promising alternative for high-density DRAM technology.

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