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Highly Reliable Ultra-Thin Ta_2O_5 Capacitor Process Technology by Using O_2-Plasma Annealing Below 400°C

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The electrical and physical properties of ultra-thin Ta_2O_5 capacitor films fabricated using O_2-plasma annealing after the film deposition are described in this paper. The O_2-plasma annealing greatly reduces the leakage current through the Ta_2O_5 capacitors, allows a low temperature of 400°C to be used, and improves TDDB characteristics compared with dry-O_2 annealing at 800°C. This is because the Ta_2O_5 films are densified by plasma ion bombardment and remain in the amorphous phase. In addition, SiO_2 layer generation between the Ta_2O_5 films and poly-silicon bottom electrodes are suppressed, so the Ta_2O_5 capacitor films have a thin SiO_2 equivalent thickness.

Introduction

Recently there has been remarkable progress in chemical vapor deposited (CVD)-tantalum penta oxide (Ta_2O_5) capacitor process technologies for high-density dynamic random access memories (DRAMs) beyond 64 Mbits. CVD-Ta_2O_5 film has a high dielectric constant and excellent step coverage characteristics. The DRAMs demand capacitor films of good leakage current characteristics and a thin SiO_2 equivalent thickness. CVD-Ta_2O_5 films are deficient in oxygen, which results in the current leak. To fill the vacancies with oxygen and to improve the electrical properties of CVD-Ta_2O_5 capacitors, some oxidization treatment is necessary after deposition, such as dry-O_2 annealing at high temperature. Therefore many researchers have studied oxidization techniques for CVD-Ta_2O_5 film after deposition[1)-5)].

Highly reliable ultra-thin capacitors were obtained by O_2-plasma annealing for oxidization of Ta_2O_5 films. The O_2-plasma annealed Ta_2O_5 capacitors have superior leakage current characteristics to dry-O_2 annealed ones. Since the O_2-plasma annealing was performed at the low temperature of 400°C, the Ta_2O_5 film was not crystallized, but remained in the amorphous phase after the annealing. In addition, the time dependent dielectric breakdown (TDDB) stress time for 50% cumulative failure was extended about 1000 times for O_2-plasma annealed Ta_2O_5 capacitors compared with those dry-O_2 annealed at 800°C.

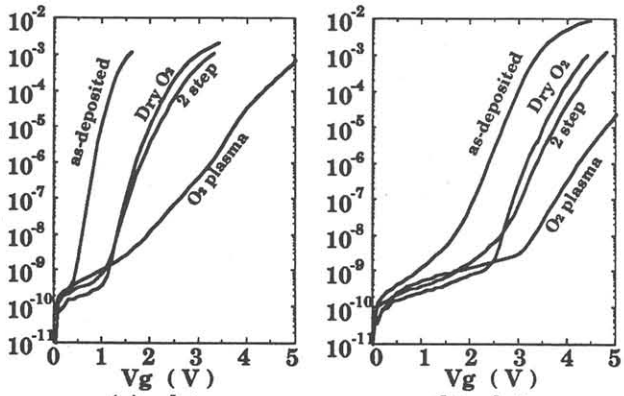
Experimental Procedure

Stacked polysilicon films were deposited and patterned to be bottom electrodes. Next rapid thermal nitridation (RTN) treatments were carried out on the surface of the bottom electrodes at 900°C for 60 seconds in NH_3 gas, just after the stacked polysilicon surface was cleaned by diluted HF. RTN treatment is an important process for reducing the SiO_2 equivalent thickness and improving the electrical properties of Ta_2O_5 capacitors[4)5)]. Ta_2O_5 films were deposited by low pressure chemical vapor deposition (LPCVD) from $Ta(OC_2H_5)_5$ and O_2. The O_2-plasma annealing was carried out at temperatures ranging from 200 to 400°C for 10 minutes, and the glow discharge was generated at 0.5 W/cm^2 using a 50 kHz RF generator. In order to compare the effect of O_2-plasma annealing with that of other methods, dry-O_2 annealing at 800°C for 10 minutes, and dry-O_2 annealing at 800°C after O_2-plasma annealing at 400°C (2-step annealing) were applied to the Ta_2O_5 films. Then, TiN plate electrodes were deposited on the Ta_2O_5 films by reactive sputtering, because the leakage current characteristics of ultra-thin Ta_2O_5 capacitors with TiN plate electrodes are far superior to those with W plate electrodes.[4)]

The electrical characteristics of the Ta_2O_5 capacitors were investigated by measuring C-V, I-V, and TDDB. The Ta_2O_5 films were analyzed using secondary ion mass spectrometry (SIMS), ellipsometry, and transmission electron microscopy (TEM).

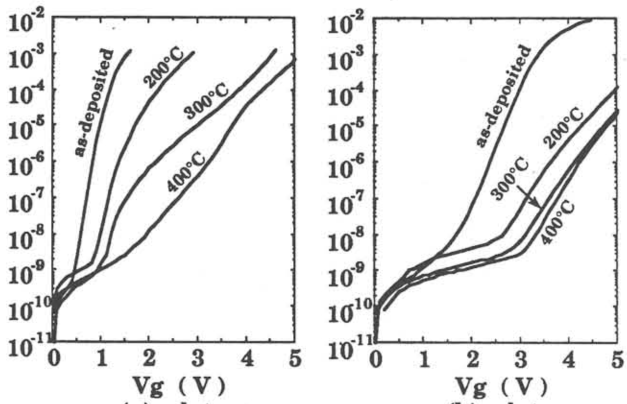
Results and Discussion

The effects of O_2-plasma annealing at 400°C on the leakage current characteristics are shown in Fig. 1. Dry-O_2 annealing suppresses the leakage current through the films, but there is an even greater improvement in the characteristics of Ta_2O_5 films by O_2-plasma annealing. It is considered that O_2-plasma annealing can fill the vacancies in the films with oxygen effectively. Figure 2 shows the dependence of the leakage current characteristics for the Ta_2O_5 films on O_2-plasma annealing temperature. With O_2-plasma annealing, the characteristics improve with the substrate temperature. The leakage current is greatly reduced at 400°C, it is 10^{-8}A/cm^2 at a bias of +1.9 V and -3.3 V.



(a) plate + (b) plate -

Fig. 1 Leakage current characteristics of the Ta2O5 capacitors.

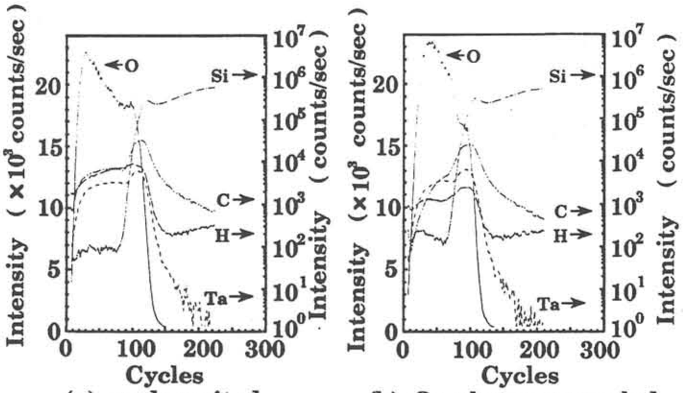


(a) plate + (b) plate -

Fig. 2 Annealing temperature dependence of the leakage characteristics for the Ta2O5 capacitor fabricated by O2 plasma

One of the reasons for the decrease in the leakage current was reported to be that the Ta_2O_5 films are densified by the elimination of carbon and hydrogen in the films[6]. SIMS depth profiles show that the amounts of carbon and hydrogen contained in the Ta_2O_5 films are decreased by O_2-plasma annealing [Fig. 3], so it is possible for O_2-plasma annealing to densify the Ta_2O_5 films.

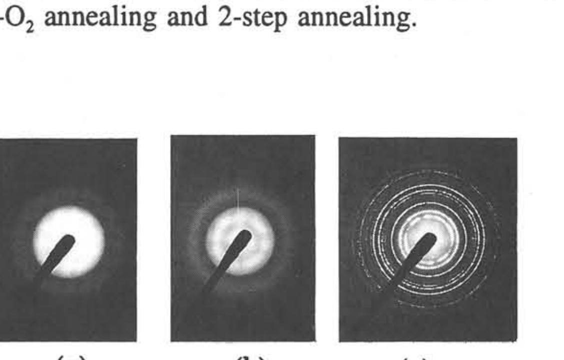
However, carbon and hydrogen are also eliminated from Ta_2O_5 films by dry-O_2 annealing, because the films emit CH_4 and H_2O gases in large quantities at about 600°C as revealed thermal desorption spectroscopy (TDS)[5]. There seems to be another reason why O_2-plasma annealing is more effective at decreasing the leakage current than dry-O_2 annealing.



(a) as-deposited (b) O2 plasma annealed

Fig. 3 Depth profiles by SIMS of as-deposited film and O2 plasma annealed film

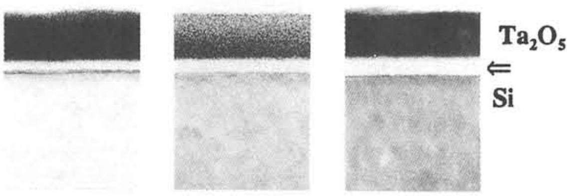
Transmission electron diffraction (TED) patterns in Fig. 4 show that the dry-O_2 annealed films are crystallized, whereas the O_2-plasma annealed films remain amorphous. The leakage current characteristics of the crystallized films are inferior to those of the amorphous films, because grain boundaries and defects in crystallized films lead to an increase in the leakage current path. The characteristics for dry-O_2 annealing after O_2-plasma annealing (2-step annealing) are deteriorated to almost the same level as those by dry-O_2 annealing. Accordingly, O_2-plasma annealing compensates for the oxygen vacancies with the films amorphous, and produces characteristics superior to be the dry-O_2 annealing and 2-step annealing.



(a) (b) (c)

Fig. 4 TED patterns of the Ta2O5 films, (a) as-deposited, (b) O2-plasma annealed, and (c) dry-O2 annealed

Figure 5(a), (b), and (c) are TEM cross section photographs of as-deposited, O_2-plasma annealed, and dry-O_2 annealed Ta_2O_5 films, respectively. Interface layers between the Ta_2O_5 films and the silicon substrates can be seen in every picture. The interface layers of as-deposited and O_2-plasma annealed samples are about 21Å and 23Å thick, respectively. These interface layers are Si_3N_4 films formed by RTN and SiO_2 films formed when Ta_2O_5 film was deposited. The thickness of the interface layer is hardly increased by O_2-plasma annealing, but the thickness is increased by about 1.5 times by dry-O_2 annealing. An increase in the interface layer thickness reduced the capacitance. Consequently, the SiO_2 equivalent thickness of the capacitor is larger with dry-O_2 annealing than O_2-plasma annealing. This is shown in figure 6. In this respect, O_2-plasma annealing is the most suitable for the fabrication of the ultra-thin Ta_2O_5 capacitors.



(a) (b) (c)
Fig. 5 TEM cross section photographs, (a) as-deposited, (b) O2-plasma annealed, and (c) dry-O2 annealed films (⇐ ; interface layer, 100Å)

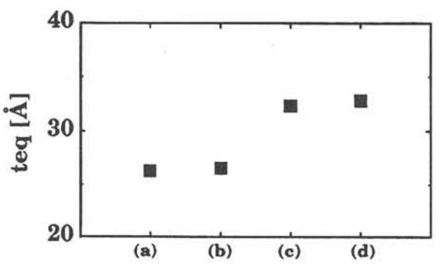


Fig. 6 Changes in teq for (a) as-deposited, (b) O2-plasma, (c) Dry-O2, and (d) 2-step annealed capacitors

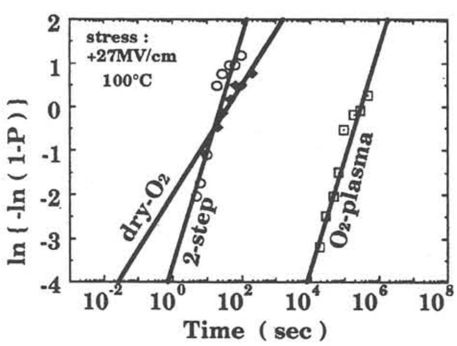


Fig. 7 TDDB stress time dependence of cumulative failure for O2-plasma, dry-O2 and 2-step

Figure 7 shows the dependence of cumulative failure on TDDB stress time for Ta_2O_5 capacitors annealed in three ways. The stress conditions for the TDDB measurement were positive bias, SiO_2 equivalent field E_{eq} (applied voltage/SiO_2 equivalent thickness) of 27 MV/cm, and a temperature of 100°C. The TDDB stress time for 50% cumulative failure for O_2-plasma annealed capacitors is about 1000 times longer than dry-O_2 annealed or 2-step annealed capacitors. Crystallization limits the TDDB characteristics of Ta_2O_5 capacitors.

Conclusion

O_2-plasma annealing of LPCVD-Ta_2O_5 capacitor films greatly improves their electrical properties. It reduces the leakage current in Ta_2O_5 films, and reduces the SiO_2 equivalent thickness of the capacitors, and extends the TDDB stress time of 50% cumulative failure about 1000 times compared with other types of annealing. The electrical properties of Ta_2O_5 capacitor films are improved because the films are densified by the elimination of carbon and hydrogen contained in the films and because oxygen vacancies are repaired. TED patterns show that O_2 plasma annealed films are amorphous, and that dry-O_2 annealed films are crystalline. This is why the O_2-plasma annealing greatly reduces the leakage current through the Ta_2O_5 films, and improves TDDB characteristics compared with dry-O_2 annealing or 2-step annealing. In addition, O_2-plasma annealing can oxidize Ta_2O_5 films without increasing their SiO_2 equivalent thickness. As a result, O_2-plasma annealing is very effective for the fabrication of highly reliable ultra-thin Ta_2O_5 capacitors fabrication.

Acknowledgments

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