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Effect of Post-Deposition Annealing and Electrode Materials on the Characteristics of Tantalum Oxide Films Deposited by Plasma-Enhanced Chemical Vapor Deposition

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A new annealing technique is proposed to improve characteristics of the tantalum oxide film for a capacitor dielectric. It is annealed in N_2O plasma gas at 400 °C for 10 minutes after plasma-enhanced chemical vapor deposition (PECVD), resulting in better current-voltage characteristics compared to the high temperature O_2 annealed film. Five kinds of capacitors have been compared by the viewpoint of the leakage current and the interfacial reaction between the tantalum oxide layer and the electrode. Poly-Si/TiN/Ta_2O_5/Si_3N_4/poly-Si capacitor structure has been found to show good electrical properties.

I. INTRODUCTION

Conventional oxide/nitride dielectric on poly-Si is still applicable to high density DRAM with three-dimensional cell architecture such as cylinder[1], fin[2], crown[3], etc. However, the trend of scaling down the device and reduction in operation voltage requires a further increase in storage capacitance to prevent soft errors[4]. In order to overcome the difficulty, ideas of increasing surface area of the storage electrode such as hemispherical grain[5] and microvillus[6] have been proposed, while thinning of the conventional dielectric film has reached effective SiO_2 thickness of 5 nm below which abrupt increase in tunneling current occurs. On the other hand, large stepheight and process complexity with the conventional capacitor are remained to be solved to realize ULSI.

High dielectric materials such as Ta_2O_5, PZT, $SrTiO_3$, $(Ba_{0.5}Sr_{0.5})TiO_3$ have been evaluated for ULSI to ensure adequate storage capacitance and to save chip cost by simplifying DRAM cell structure. Among them, the tantalum oxide is regarded as the most promising storage dielectric, even though it still has unsolved problems.

This paper describes a new annealing technique to improve characteristics of the tantalum oxide film for a storage dielectric. Effects of electrode materials have also been compared by the viewpoint of current-voltage characteristics and interfacial reaction between the tantalum oxide and the electrode: poly-Si, Si_3N_4/poly-Si and W for a storage electrode and Al, Al/TiN, and poly-Si/TiN for a plate electrode.

II. EXPERIMENTAL

Ta_2O_5 films of 15 nm in thickness were deposited by PECVD using tantalum ethylate ($Ta(C_2H_5O)_5$) and nitrous oxide (N_2O). The liquid source of tantalum ethylate was vaporized at 140 °C and was transferred through the gas line kept at 180 °C into the reaction chamber by argon gas. The total gas pressure was maintained at 1.5 torr and the wafer temperature at 400 °C and the RF power at 300 W. The spacing between the wafer and the upper electrode was fixed at 25 mm. The deposition rate was around 1.5 nm/min.

The tantalum oxide film was in-situ annealed in the N_2O plasma environment at 400 °C for 10 minutes after PECVD. The flow rate of N_2O gas was set at 7slm.

Five kinds of capacitors were prepared on (100) oriented p-type silicon wafers:

a) Al/Ta_2O_5/poly-Si
b) Al/Ta_2O_5/W
c) Al/TiN/Ta_2O_5/poly-Si
d) poly-Si/TiN/Ta_2O_5/poly-Si
e) poly-Si/TiN/Ta_2O_5/Si_3N_4/poly-Si

Microstructure of the tantalum oxide was investigated by TEM and FTIR analysis before and after different annealing treatments of the film. The degree of crystallinity of the tantalum oxide film after high temperature annealing treatments was examined through the measurement of refractive index by ellipsometry and FTIR peak intensity. TEM and SIMS were also used to examine the interfacial layer between the

tantalum oxide film and the electrode materials. The electrical properties of the tantalum oxide film were characterized by capacitance-voltage and current-voltage measurement.

III. RESULTS and DISCUSSION

Fig.1 shows current-voltage characteristics of Ta_2O_5 films annealed at two different conditions: high temperature (800 °C) O_2 annealing and N_2O plasma annealing. The difference in current-voltage characteristics can be explained by the viewpoint of reduced defect densities and microstructural change from amorphous to crystalline by the high temperature annealing treatment. Grain boundaries and grooves at the surface of the crystalline film lead to larger leakage current compared to the N_2O plasma annealed film whose structure is amorphous.

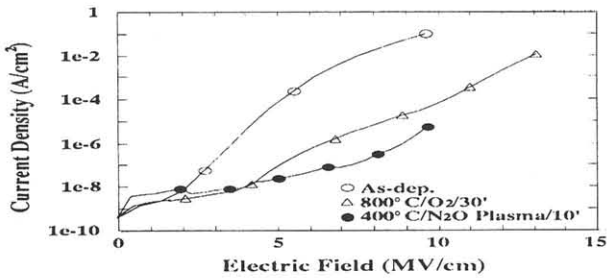

Fig.1 Current-voltage characteristics of the Ta_2O_5 capacitors before and after annealing treatments:400 °C/ N_2O plasma/10 min. and 800 °C/O_2/30 min.

Microstructural changes of the films were investigated by TEM, FTIR, and R.I. measurements. Fig.2 shows TEM cross sections and diffraction patterns of the films with four different annealing treatments: (a) 400 °C / N_2O plasma / 10 min., (b) 700 °C / N_2 / 30 min., (c) 800 °C / N_2 / 30 min., (d) 900 °C / N_2 / 30 min. The crystallinity of the tantalum oxide film increased with the annealing temperature, while the amorphous structure of as-deposited film remained unchanged after the N_2O plasma treatment. The grain boundaries and the grooves at the surface are clearly shown in Fig.2 (c) and (d). The R.I. change as shown in Fig.(3) proved increase in the crystallinity of the film with the annealing temperature. Fig.(4) shows FTIR spectra of the films which again confirmed appearance of the crystalline structure with the high temperature annealing. The peak at the wave number of about 510 cm^{-1} indicates the crystalline structure of the tantalum oxide, while the peak around 635 cm^{-1} the amorphous one. Vacancy defects[7] of as-deposited film were supposed to be filled during the N_2O plasma annealing by the excited oxygen atoms at the N_2O plasma state.

Fig.5 shows current-voltage characteristics of the capacitors with different storage electrodes. Sample (a) with poly-Si storage electrode has less leakage current

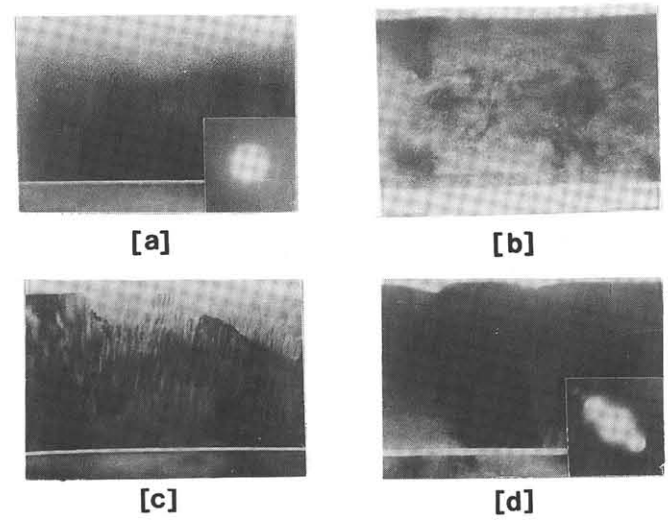

Fig.2 TEM cross sections and diffraction patterns of the Ta_2O_5 films with four different annealing treatments: (a) 400 °C/N_2O plasma/10 min., (b) 700 °C/N_2/30 min., (c) 800 °C/N_2/30 min. (d) 900 °C/N_2/30 min.

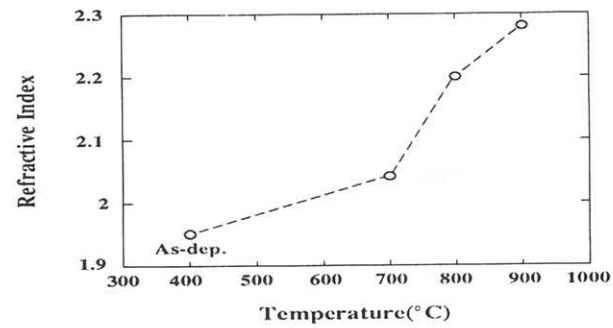

Fig.3 Change of refractive index with high temperature N_2 annealing of Ta_2O_5 films.

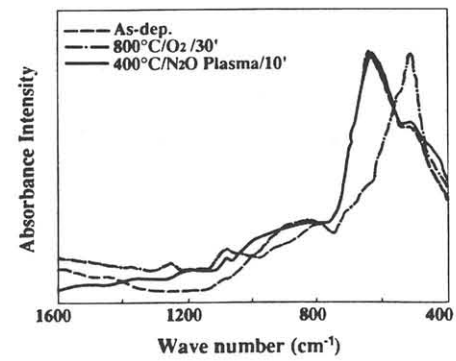

Fig.4 FTIR spectra of Ta_2O_5 films before and after annealing treatments: 400 °C / N_2O plasma / 10 min. and 800 °C / O_2 / 30 min.

than sample (b) with W electrode due to the fact that a SiO_2 interfacial layer was formed between the tantalum oxide and the poly-Si and the W electrode was oxidized during the 800 °C / O_2 / 30 min. annealing treatment. The SiO_2 film thickness was found to be around 2nm. The SiO_2 film improves the leakage current of the capacitor, while the oxidation of W

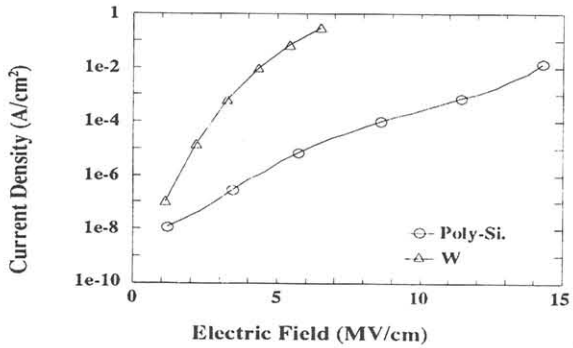

Fig.5 Current-voltage characteristics of the Ta_2O_5 capacitors with different storage electrodes: W and poly-Si.

degrades it. Diffusion of oxygen atoms to W electrode through the tantalum oxide and oxidation of W electrode was revealed by SIMS analysis. Fig.6 shows depth profile of the oxygen atom for sample (b) after the 800 °C / O_2 / 30 min. annealing treatment.

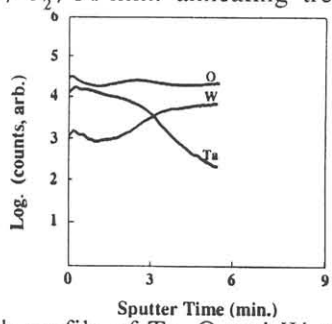

Fig.6 Depth profile of Ta, O and W atoms for the Al/ Ta_2O_5/W capacitor after the 800 °C/O_2/30 min. annealing treatment.

Fig.7 shows effects of the plate electrode materials on the current-voltage characteristics. The addition of TiN layer as in sample (c) and (d) improves the leakage current compared to sample (a). S. Kamiyama, et al.[8] described that it is due to the compensation of the electrical trap sites in the Ta_2O_5 with Ti atoms.

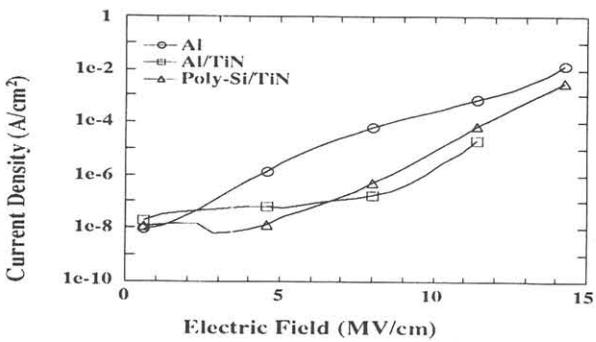

Fig.7 Current-voltage characteristics of the Ta_2O_5 capacitors with different plate electrodes: Al, Al/TiN and poly-Si/TiN.

The leakage current of sample (d) can be more reduced by RTN treatment of the SiO_2 film on the poly-Si storage electrode before deposition of the tantalum

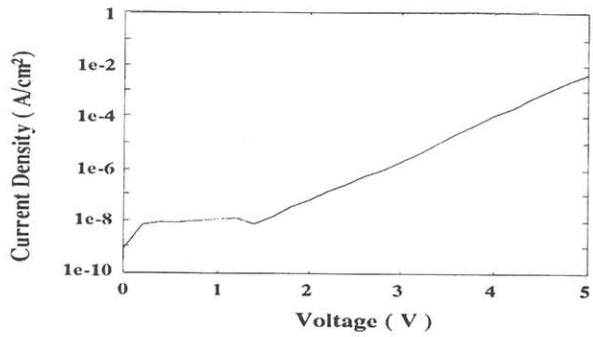

Fig.8 Current-voltage characteristics of the poly-Si/TiN/ Ta_2O_5/Si_3N_4/poly-Si capacitor with the RTN treatment of the SiO_2 film on the poly-Si storage electrode.

oxide film. The nitride layer also prevents an interaction of the tantalum oxide and the poly-Si storage electrode during the subsequent high temperature processes. Fig.8 shows the current-voltage characteristics of sample (e). It indicates that the leakage current at $1/2V_{cc}$ = 1.0 V is suitable for 256Mbit DRAM.

IV. CONCLUSION

The leakage current of the tantalum oxide was more reduced by a new annealing treatment in comparison with the high temperature O_2 annealing: N_2O plasma annealing at 400 °C for 10 min. It is due to the retained amorphous structure of as-deposited film as well as reduced defect densities. RTN treatment of the SiO_2 film on the storage electrode and TiN deposition on the tantalum oxide before deposition of the plate electrode are considered to be essential to improve the leakage current of the capacitor. At present, poly-Si/ TiN/Ta_2O_5/Si_3N_4/poly-Si capacitor structure seems to be the most promising one for ULSI.

ACKNOWLEDGEMENT

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