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Optimum Electrode Materials for Ta_2O_5 Capacitors at High and Low Temperature Processes

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In this paper, we describe the effects of electrode materials on the leakage current of Ta_2O_5 films, and show optimum electrode materials at high- and low-temperature processes. The leakage current depends on the electrode material and varies with the annealing temperature. The leakage current is mainly determined by the work function of the electrode before and after low-temperature annealing (400 °C). On the other hand, after high-temperature annealing (800 °C), the leakage current is also affected by the reaction between Ta_2O_5 and the electrode. From the viewpoint of the leakage current, TiN and Mo (or MoN) are optimum materials for low- and high-temperature processes, respectively.

1. INTRODUCTION

Tantalum oxide (Ta_2O_5) has been studied extensively as a candidate for a very thin capacitor dielectric film in future DRAM's. It is reported that the electrical characteristics of Ta_2O_5 films greatly depend on the deposition condition [1], the oxidation condition [2-4] of Ta_2O_5 films, and the top electrode material [1, 2], e.g., Al, Au, W and TiN. In these reports, the leakage current was measured just after deposition of the top electrode. However, in the practical fabrication process, several annealing processes, such as the annealing of Al in H_2 (about 400 °C) and flow of BPSG (boro-phospho silicate glass) films in N_2 (about 800 °C), exist after the deposition of the top electrode. For this reason, the electrode material must be determined in considering the characteristics of Ta_2O_5 films after these annealing processes.

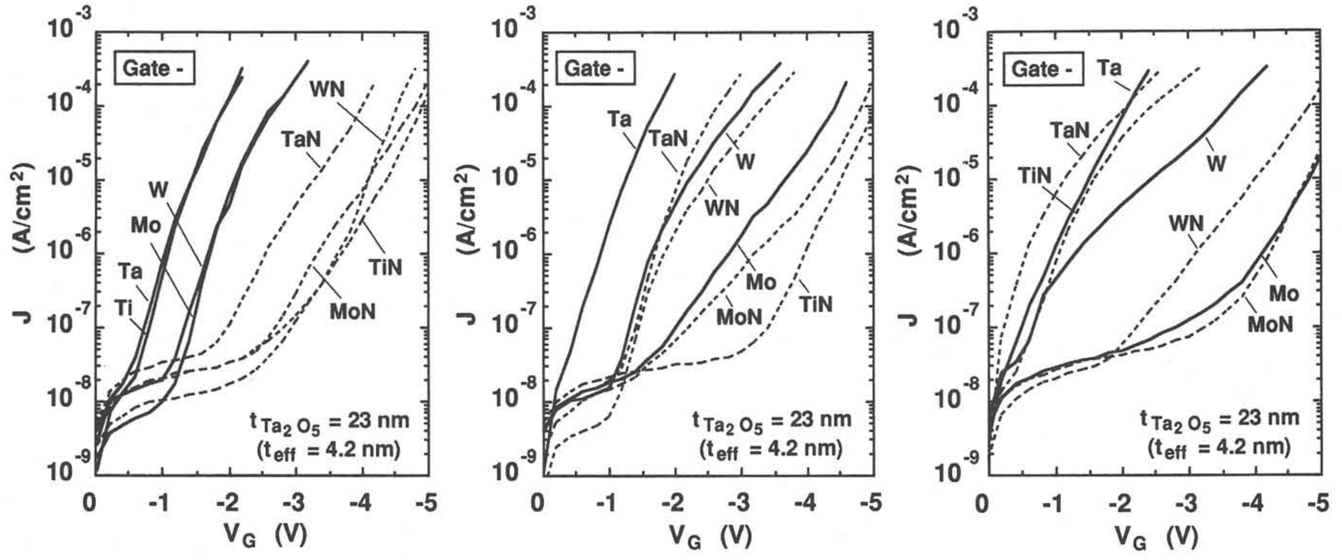
In this study, we investigate the effects of electrode materials, metals (W, Mo, Ti and Ta) and their nitrides (WN, MoN, TiN and TaN), on the leakage current in Ta_2O_5 films before and after annealing, and propose optimum electrode materials at high- and low-temperature processes.

2. EXPERIMENTAL

Ta_2O_5 films were deposited on n^+ poly-Si by low-pressure chemical vapor deposition (LPCVD) using $Ta(C_2H_5O)_5$ and O_2 at 400 °C. Then, Ta_2O_5 films were annealed in dry O_2 at 800 °C for 60 s. The metal (W, Mo, Ti and Ta) and nitride (WN, MoN, TiN and TaN) electrodes were deposited on Ta_2O_5 films through a dot mask by sputtering and reactive sputtering (20% N_2/Ar), respectively. In order to investigate the effects of annealing after deposition of the top electrode, these samples were annealed in N_2 for 30 min at 400 and 800 °C. The electrical characteristics of the Ta_2O_5 films were measured by I-V, and C-V methods. The reaction of the electrode materials with Ta_2O_5 film was analyzed by secondary ion mass spectroscopy (SIMS).

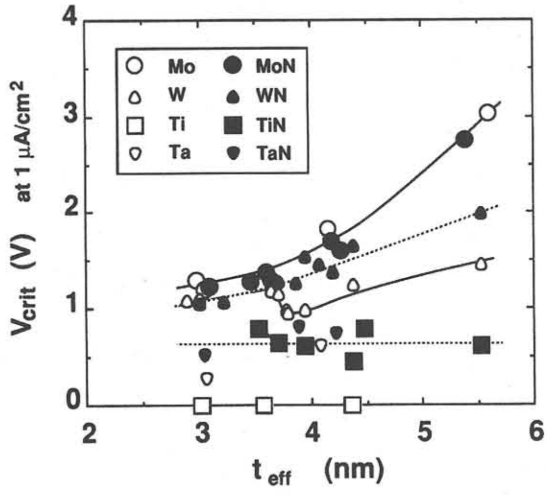
3. RESULTS AND DISCUSSION

Figure 1 shows the leakage current characteristics (J -V_G) of Ta_2O_5 capacitors with several electrode materials before and after annealing. The negative bias was applied to the top electrode. Before annealing, the leakage currents of capacitors with nitride electrodes are smaller than those with metal ones. Upon low-temperature annealing (400 °C), the leakage currents of capacitors with WN, MoN and TaN increase, but that with TiN is unchanged. Before and after annealing at 400 °C, the leakage current of the capacitor with TiN is the smallest among these capacitors. However, after high-temperature annealing (800 °C), the leakage current of the capacitor with TiN greatly increases. On the other hand, the capacitor with Mo or MoN shows the smallest leakage current, which is smaller than that before annealing. Figure 2 shows the dependence of the critical voltage (V_{crit}) on the effective SiO_2 thickness (t_{eff}) after 800 °C annealing. V_{crit} is defined as the voltage which

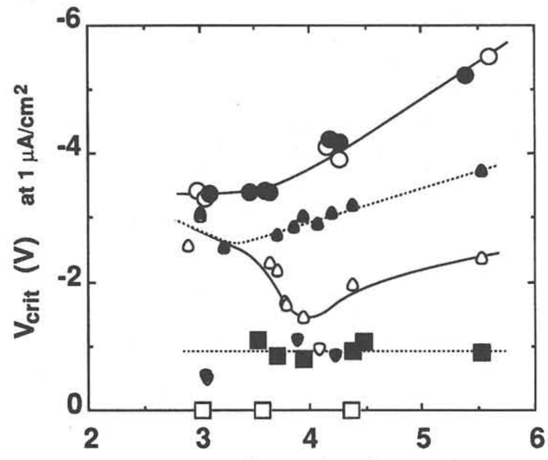


(a) Before annealing (b) After 400 °C annealing (c) After 800 °C annealing

Fig.1 Leakage current characteristics of CVD-Ta_2O_5 capacitors with several electrode materials.



(a) Gate +



(b) Gate -

Fig.2 Dependence of critical voltage(V_{crit}) on effective SiO_2 thickness (t_{eff}) after 800 °C annealing.

Table I Work function (ϕ_m) of electrode materials before and after annealing.

Electrode materials	Work function ϕ_m (eV)		
	Before Annealing	400 °C annealing	800 °C annealing
Mo	4.64	4.78	4.94
W	4.75	4.74	4.77
Ti	4.17	3.91	—
Ta	4.25	4.33	4.72
MoN	5.33	4.89	4.70
WN	5.00	4.76	4.83
TiN	4.95	4.80	4.81
TaN	5.41	4.55	—

induces a leakage current of 1 μA/cm^2. It is found that the values of V_{crit} for Mo and MoN all show the maximum value for any t_{eff} at each gate bias.

In order to verify the effects of electrode materials on the leakage current, the work function (ϕ_m) of the electrode was evaluated (Table I). ϕ_m is calculated from the relationship between the flatband voltage and the SiO_2 thickness of MOS (electrode/SiO_2/Si) capacitors. [5] It is found that ϕ_m is different in each material and at each annealing temperature. For the purpose of comparing ϕ_m with the leakage current, the relationship between ϕ_m and V_{crit} for samples shown in Fig. 1 is plotted in Fig. 3. It is found that, in most electrode materials, V_{crit} increases with increasing ϕ_m before and after annealing at 400 °C. In other words, the leakage current in the Ta_2O_5 film decreases with increasing ϕ_m. I-V characteristics for a Ta_2O_5 film were explained in

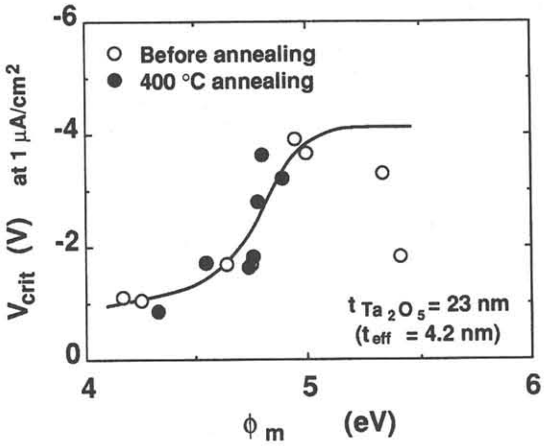


Fig.3 Relationship between ϕ_m and V_{crit} for samples shown in Fig.1

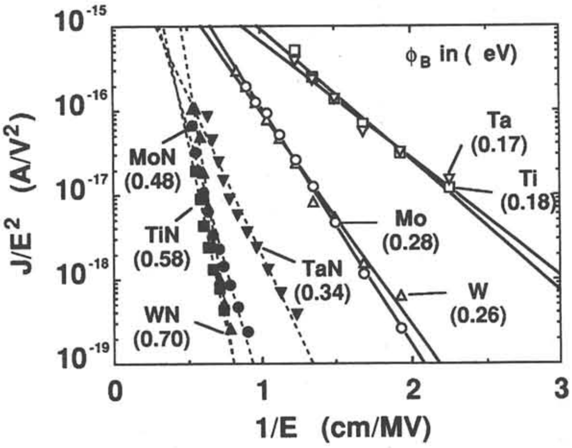


Fig.4 Fowler-Nordheim plot for sample shown in Fig.1 before annealing.

terms of several conduction mechanisms, such as Poole-Frenkel (PF) conduction [6], trap-assisted tunneling [6], Fowler-Nordheim (FN) tunneling [7] and hopping conduction [7]. I-V characteristics in this experiment cannot be explained by PF or hopping conduction because the leakage current depends on electrode materials. Figure 4 shows the FN plot for samples shown in Fig.1 before annealing. In this figure, ϕ_B is the energy difference between the work function of the top electrode and the conduction band of Ta_2O_5 and is calculated from a slope of lines. It is found that the data for each material are on one line and that ϕ_B increases with increasing ϕ_m of electrode materials. These relationships are the same as those after annealing at 400 °C. These results suggest that the barrier height for electrons at the electrode/Ta_2O_5 interface limits the leakage current. However, the value of ϕ_B in this experiment is much smaller than the theoretical value [7]. It may be suggested that the current conduction is dominated by trap-assisted tunneling. On the other

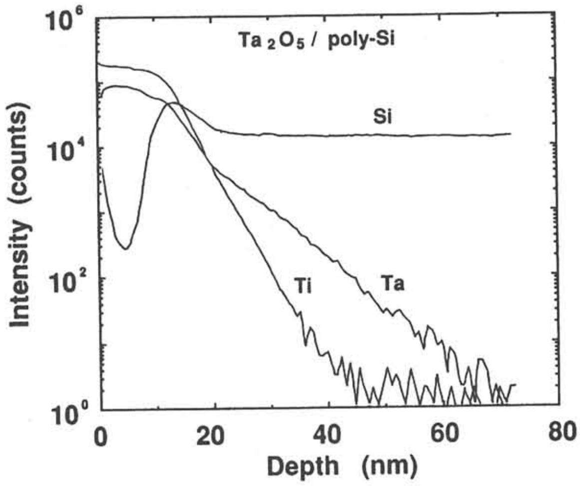


Fig.5 SIMS depth profiles of elements in Ta_2O_5 film after removing TiN after 800 °C annealing.

hand, after 800 °C annealing, there is almost no correlation between the work function and the leakage current. It is considered that, after high-temperature annealing, the leakage current is affected by the reaction between Ta_2O_5 and the electrode. Figure 5 shows SIMS depth profiles of elements in the Ta_2O_5 film after removing the TiN electrode after 800 °C annealing. It is found that Ti is uniformly diffused into Ta_2O_5. This indicates that TiN reacts with Ta_2O_5 at 800 °C and this reaction induces the increase of the leakage current. From these results, we consider that the reason why capacitors with Mo or MoN show a small leakage current is mainly due to the high stability of the electrode/Ta_2O_5 interface at high-temperatures.

4. CONCLUSIONS

This paper shows that the work function of the top electrode material and the stability of the electrode/ Ta_2O_5 interface determine the electrical characteristics of the Ta_2O_5 film, and that TiN is the optimum electrode for low-temperature process (about 400 °C) while Mo or MoN is the optimum electrode for high-temperature process (about 800 °C).

REFERENCES

[1] M. Saitou et al. : IEDM Tech. Dig. (1986) p.680
[2] S. Kamiyama et al. : IEDM Tech. Dig. (1991) p.827
[3] H. Shinriki et al. : VLSI Symp. (1989) p.25
[4] H. S. Park et al. : SSDM Ext. Abs. (1992) p.524
[5] H. Matsuhashi et al. : Jpn. J. Appl. Phys. 28 (1989) L2309
[6] H. Shinriki et al. : SSDM Ext. Abs. (1991) p.198
[7] S. Zaima et al. : J. Electrochem. Soc. 137 (1990) p.2876