Optimum Electrode Materials for Ta2O5 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 Ta2O5 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 Ta2O5 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 (Ta2O5) 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 Ta2O5 films greatly depend on the deposition condition [1], the oxidation condition [2-4] of Ta2O5 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 H2 (about 400 °C) and flow of BPSG (boro-phospho silicate glass) films in N2 (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 Ta2O5 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 Ta2O5 films before and after annealing, and propose optimum electrode materials at high- and low-temperature processes.

2. EXPERIMENTAL

Ta2O5 films were deposited on n⁺ poly-Si by low-pressure chemical vapor deposition (LPCVD) using Ta(C2H5O)5 and O2 at 400 °C. Then, Ta2O5 films were annealed in dry O2 at 800 °C for 60 s. The metal (W, Mo, Ti and Ta) and nitride (WN, MoN, TiN and TaN) electrodes were deposited on Ta2O5 films through a dot mask by sputtering and reactive sputtering (20% N2/Ar), respectively. In order to investigate the effects of annealing after deposition of the top electrode, these samples were annealed in N2 for 30 min at 400 and 800 °C. The electrical characteristics of the Ta2O5 films were measured by I-V, and C-V methods. The reaction of the electrode materials with Ta2O5 film was analyzed by secondary ion mass spectroscopy (SIMS).

3. RESULTS AND DISCUSSION

Figure 1 shows the leakage current characteristics (J-V) of Ta2O5 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 (Vcrit) on the effective SiO2 thickness (tSiO2) after 800 °C annealing. Vcrit is defined as the voltage which
induces a leakage current of 1 μA/cm². 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 (\( \phi_m \)) of the electrode was evaluated (Table I). \( \phi_m \) is calculated from the relationship between the flatband voltage and the SiO₂ thickness of MOS (electrode/SiO₂/Si) capacitors. [5] It is found that \( \phi_m \) is different in each material and at each annealing temperature. For the purpose of comparing \( \phi_m \) with the leakage current, the relationship between \( \phi_m \) 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 \( \phi_m \) before and after annealing at 400 °C. In other words, the leakage current in the Ta₂O₅ film decreases with increasing \( \phi_m \).

I-V characteristics for a Ta₂O₅ film were explained in

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**Fig. 1** Leakage current characteristics of CVD-Ta₂O₅ capacitors with several electrode materials.

**Table I** Work function (\( \phi_m \)) of electrode materials before and after annealing.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Work function ( \phi_m ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before 400 °C annealing</td>
</tr>
<tr>
<td>Mo</td>
<td>4.64</td>
</tr>
<tr>
<td>W</td>
<td>4.75</td>
</tr>
<tr>
<td>Ti</td>
<td>4.17</td>
</tr>
<tr>
<td>Ta</td>
<td>4.25</td>
</tr>
<tr>
<td>MoN</td>
<td>5.33</td>
</tr>
<tr>
<td>WN</td>
<td>5.00</td>
</tr>
<tr>
<td>TiN</td>
<td>4.95</td>
</tr>
<tr>
<td>TaN</td>
<td>5.41</td>
</tr>
</tbody>
</table>

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**Fig. 2** Dependence of critical voltage(\( V_{crit} \)) on effective SiO₂ thickness (\( t_{eff} \)) after 800 °C 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, $\phi_B$ is the energy difference between the work function of the top electrode and the conduction band of Ta$_2$O$_5$ and is calculated from a slope of lines. It is found that the data for each material are on one line and that $\phi_B$ increases with increasing $\phi_m$ 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$_2$O$_5$ interface limits the leakage current. However, the value of $\phi_B$ 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 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$_2$O$_5$ and the electrode. Figure 5 shows SIMS depth profiles of elements in the Ta$_2$O$_5$ film after removing the TiN electrode after 800 °C annealing. It is found that Ti is uniformly diffused into Ta$_2$O$_5$. This indicates that TiN reacts with Ta$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ interface determine the electrical characteristics of the Ta$_2$O$_5$ 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