The effects of thermal N₂ annealing on the passivation capability of sputtered Ta and Ta-nitride (Ta(-N)) layers against Cu oxidation in a 200 Å Ta(-N) covered Ta(-N)/Cu/SiO₂/Si structures was investigated. The N₂ annealed Ta layers revealed degradation in passivation capability, presumably due to grain growth of the Ta passivation layer. In contrast, the nitrogen-doped Ta-nitride layers showed a contrary trend. For the Ta-nitride layer with 23.5 atom % of nitrogen, passivation capability was effectively improved by N₂ annealing at 300°C. For the Ta-nitride layer with 30.5 atom % of nitrogen, N₂ annealing at higher temperatures (500–700°C) was necessary to improve the passivation capability. The healing of sputtering damage of Ta-nitride passivation layers by the thermal N₂ annealing was responsible, presumably, for the improvement of passivation capability.

Results and Discussion
The passivation capability of 200 Å Ta and Ta-nitride layers for the Ta(-N) covered Ta(-N)/Cu/SiO₂/Si structures in an oxidizing ambient was investigated in a previous study by the authors. It was also found that N₂ annealing of these Ta(-N) layers did not change the chemical states and the atomic concentrations of tantalum and nitrogen. In the current study, the effects of N₂ annealing on the passivation capability of the Ta(-N) layers were examined.

Table I. Sputtering condition and nitrogen content of as-deposited Ta and Ta-nitride films.

<table>
<thead>
<tr>
<th>Sample identification</th>
<th>A (Ta)</th>
<th>B (Ta-nitride)</th>
<th>C (Ta-nitride)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial pressure of N₂ in sputtering gas (mTorr)</td>
<td>0</td>
<td>1.52</td>
<td>2.4</td>
</tr>
<tr>
<td>Deposition power (W)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Deposition rate (Å/s)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrogen atomic concentration (%)</td>
<td>23.5</td>
<td>30.5</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Summary of sample identification and N₂/O₂ annealing temperatures.

<table>
<thead>
<tr>
<th>A samples</th>
<th>B samples</th>
<th>C samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ annealing</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>300°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>500°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>700°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>O₂ annealing</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>350°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>400°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>450°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
<tr>
<td>500°C</td>
<td>Bₐ₋₅N₃₅₀₀</td>
<td>Cₐ₋₅N₃₅₀₀</td>
</tr>
</tbody>
</table>

Ta Passivation Layers

A samples.—Figure 1 shows the XRD spectra of 400°C O₂ annealed A samples. Signals of the CuO phase appeared only in the spectrum of A₇N₄₀₀₀ sample. Also, the sheet resistance measured of this sample was eight times larger than that of the other samples, indicating the oxidation of Cu in this sample.

Figure 2 shows the SIMS depth profiles of A samples. There was not much structural difference between samples A₄₀₀₀ and A₅N₄₀₀₀. However, the A₇N₄₀₀₀ samples showed a significant change in elemental depth profiles, indicating the degradation of passivation capability resulting from a 700°C N₂ annealing.

Figure 3 shows the XPS depth profiles of compositional elements and the binding energy spectra of Cu 2p₃/2 photoelectrons for the A₄₀₀₀ and A₅N₄₀₀₀ samples. A

![Fig. 1. XRD spectra of 400°C O₂ annealed A samples.](image1)

![Fig. 2. SIMS depth profiles of compositional elements for the samples (a) A₄₀₀₀, (b) A₅N₄₀₀₀, and (c) A₇N₄₀₀₀.](image2)

![Fig. 3. XPS depth profiles of compositional elements and XPS binding energy spectra of Cu 2p₃/2 photoelectrons for the samples (a) A₄₀₀₀ and (b) A₅N₄₀₀₀.](image3)
copper oxide phase of CuO was identified in the spectrum of $A_{3N4000}$ (Fig. 3b, cycles 0) but not in the spectrum of $A_{3N4000}$ (Fig. 3a). The degradation of passivation capability for the Ta passivation layer due to N$_2$ annealing can be more clearly observed on the SEM micrographs shown in Fig. 4, in which CuO clusters$^{22,30,36}$ are present on the surface of N$_2$ annealed samples. The copper oxide phase of CuO was also determined by the XPS analysis for the sample of $A_{3N4000}$. In fact, the degradation occurred due to N$_2$ annealing at temperatures as low as 300°C.

The degradation of passivation capability of Ta passivation layer is presumably caused by the grain growth of the thin Ta passivation layer. Figures 5 and 6 show, respectively, the XRD spectra and the surface morphology for A samples with and without N$_2$ annealing. The $\beta$Ta signal was detected on sample $A_{3N}$ (Fig. 5) and Ta flaking was observed on the surface of sample $A_{3N}$ as well as $A_{7N}$ (Fig. 6b). As the grain size became compatible with the film thickness, shorter diffusion paths$^{14,20,34,35}$ were built along the grain boundaries and the voids,$^{34,35}$ leading to degradation of passivation capability.

**Ta-Nitride Passivation Layers**

$B$ Samples.—Figure 7 shows the XRD spectra of 450°C O$_2$ annealed B samples. No copper oxide phase was observed by the XRD analysis. After the O$_2$ annealing at 450°C, the sheet resistance remained constant for all B samples except sample $B_{3N}$, which showed a 150% increase in sheet resistance as compared with that of sample $B_{3N}$. Figure 8 illustrates the AES depth profiles of as-deposited and 450°C O$_2$ annealed B samples. The passivated Cu film and the Ta-nitride passivation layer for the N$_2$ annealed samples (Fig. 8c, d, and e) remained basically unchanged as
CuO(-111) CuO(200)

Fig. 7. XRD spectro of 450°C O2 annealed B samples.

compared with those of the as-deposited sample B0 (Fig. 8a); however, complete intermixing of Cu, Ta, and O occurred for the sample of Bn4500 (Fig. 8b), which did not go through N2 annealing. Figure 9 shows the results of the XPS analysis. The Cu 2p3/2 photoelectrons were detected on the surface of sample B04500 (Fig. 9a), and were identified to be in the state of CuO. The XPS spectra of Cu 2p3/2 photoelectrons for sample Bn4500 in the surface region and under the Ta-nitride layer are illustrated in Fig. 9b. No detectable Cu photoelectron was found in the surface region and the Ta-nitride layer. The Cu 2p3/2 photoelectrons found under the Ta-nitride passivation layer were determined to be in the elemental state. For sample Bn4500, the only oxide phase detected by the XPS was Ta2O5 existing in the outermost surface region. Under the Ta2O5 layer, Ta 4f7/2 and N is photoelectrons remained in their nitride phase as were in the as-deposited sample.35

The N2 annealing process for B samples effectively improved the passivation capability of their passivation lay-

ers. And the superiority of passivation capability of sample Bn over that of sample A was presumably due to amorphism34-36 of the Ta-nitride layer. Figure 10 shows the surface morphology for the as-deposited Ta-nitride (or TaN)38 layer (Fig. 10a) as well as the 700°C N2 annealed film (Fig. 10b). No obvious grain growth of Ta-nitride was observed. This implies the fine grain of the Ta-nitride film and thus a long diffusion path for Cu along the grain boundaries. The thermal N2 annealing healed the micro-damage in the reactively sputtered Ta-nitide layer,35 however, it resulted in new defects, i.e., void formation, as shown in Fig. 6b and 10b. Thus, the passivation improvement was limited to thermal annealing in O2 ambient at 450°C. It was found that none of samples A or B, either with or without N2 annealing, can withstand a thermal annealing in O2 ambient at 500°C for 50 min without the Cu film being oxidized.

Fig. 8. AES depth profiles of compositional elements for the samples (a) B, (b) Bn4500, (c) B04500, (d) Bn4500, and (e) Bn4500.

Fig. 9. XPS spectra showing (a) surface compositional elements survey for the sample Bn4500 and (b) binding energy spectrum of Cu 2p3/2 photoelectrons for the sample Bn4500 on the outermost surface as well as under the Ta-nitride passivation layer.

(c) Bn4500

Cu2O(-111) Cu2O(200)

\[ \text{Cu2O}(-111) \rightarrow \text{Cu2O}(200) \]

Fig. 10. XRD spectro of 450°C O2 annealed B samples.
the thermal O₂ annealing at 400°C, N₂ annealing at temperatures above 700°C was needed. Figure 13 illustrates the AES depth profiles for C samples thermally annealed in O₂ ambient at 350°C. For samples C₃5000 and C₅35000, Cu was oxidized partially and the Ta-nitride passivation layer was covered with a layer of CuO (Fig. 13a and b). The extent of Cu oxidation was reduced by raising the N₂ annealing temperature to 700°C (Fig. 13c). Figure 14 shows the SIMS depth profiles for C samples thermally annealed in O₂ ambient at 400°C. For sample C₄40000, the original structure of Ta-nitride/ Cu/SiO₂/Si was destroyed and copper oxide can be seen clearly (Fig. 14a). Similar results were observed for the samples with N₂ annealing at temperatures below 700°C. For samples C₅40000 and C₇40000, which were annealed in N₂ at 700 and 800°C, respectively, the original structure of Ta-nitride/Cu/SiO₂/Si retained its integrity (Fig. 14b and c). Figure 15 shows the XPS survey spectra of surface elements for the C samples. Only the samples annealed in N₂ at 700°C did not reveal Cu 2p photoelectrons which were determined to be CuO phase. From the above
observation, we conclude that the passivation capability of C samples, can be improved by N₂ annealing at temperatures above 700°C.

Figure 16 shows the XRD spectra of as-deposited and thermally N₂ annealed C samples. A small peak belonging to the Ta-nitride phase appeared in the C₇N₃500 spectrum. Similar to B samples, the thermal N₂ annealing did not result in the change of atomic concentration and chemical state of Ta and N in C samples. A comparison of the surface morphologies of the as-deposited sample C₅N and the 700°C N₂ annealed sample C₇N is shown in Fig. 17. N₂ annealing at 700°C resulted in no obvious grain growth. The amorphism of the Ta-nitride films of C samples is similar to that of B samples. However, the void formation (Fig. 17b) prohibited further improvement on the passivation capability by thermal N₂ annealing at higher temperatures.

To improve passivation capability, an N₂ annealing at 300°C would be beneficial to sample B, but a 700°C N₂ annealing was necessary for sample C to be effective. The differences lies in the degree of sputtering damage between sample B₅ and sample C₅. For the as-deposited sample C₅, visible damage resulting from energetic N₂ plasma during sputtering was observed (Fig. 17a). We presumed that the sputtering induced damage was responsible for the inferior passivation capability of sample C₅ as compared with sample B₅. The improvement of passivation capability for the high temperature N₂ annealed C samples was principally due to sputtering damage healing.

Conclusion
This work studied the effects of thermal N₂ annealing on the passivation capability of sputtered Ta and Ta-nitride layers against Cu oxidation in a 200 Å Ta(-N) covered Ta(-N)/Cu/SiO₂/Si structure. For Ta passivation layers, the Ta/Cu/SiO₂/Si structure was able to sustain a thermal annealing in O₂ ambient at 400°C for 50 min without Cu oxidation. However, N₂ annealing at temperatures of 300°C and above resulted in the degradation of passivation capability. This is, presumably, because thermal N₂ annealing resulted in grain growth for the Ta passivation layer, leading to shorter paths of diffusion for Cu along the grain boundaries. The N-doped Ta-nitride layers revealed an opposite effect on passivation capability with respect to N₂ annealing. For the Ta-nitride layer of sample B (with 23.5 atom % nitrogen in Ta-nitride), passivation capability was effectively improved by the N₂ annealing process at 300°C. The N₂ annealed sample was able to sustain thermal annealing in O₂ ambient at temperatures up to 450°C without Cu oxidation. Moreover, the higher the N₂ annealing temperature was, the better the result of passivation became. For the Ta-nitride layer of sample C (with 30.5
atom % nitrogen in Ta-nitride), N, annealing at higher temperatures of 500 to 700°C was needed for the improvement to be effective because the as-deposited Ta-nitride layer was more seriously damaged. The sputtering damage healing of Ta-nitride passivation layers of sample B and sample C by the thermal N2 annealing was, presumably, responsible for the improvement of passivation capability.

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