Integration of CVD W- and Ta-based Liners for Copper Metallization

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Both TaNx and WNx are candidates for copper liner applications. A thermal CVD process for the deposition of WNx liners, as well as both thermal CVD and plasma-assisted CVD processes for the deposition of TaNx, have been developed, all of which are carried out at wafer temperatures under 425°C. The basic material properties, conformality, thermal stability, and integration and diffusion barrier properties of these materials make them appropriate for use in advanced copper-based interconnect applications.

Due to copper's high diffusivity into Si and SiO2 and poor adhesion to most dielectric materials, refractory metal-based liners such as TiN, Ta, TaNx, and WNx are used to chemically isolate the copper from the dielectric. In particular, TaNx (where x corresponds to a slightly nitrogen-rich stoichiometry) and WNx (where x=0.5) appear to possess sufficient barrier properties for upcoming device generations.

Because of the high aspect ratios and complex geometries that will be encountered in advanced dual-damascene structures, liner conformality is of primary importance. Poor liner conformality requires deposition of a thicker liner to achieve a given bottom or sidewall liner thickness. Thicker liners increase the effective resistance of the line and, in more aggressive structures, lead to nonuniform Cu nucleation and poor filling. Advanced PVD processes such as ionized metal plasma (IMP) TaNx can extend sputtering for a few more device generations, but it is believed that a CVD liner solution will likely be required for such applications.

WF6-based CVD and plasma-assisted CVD processes for WNx have been reported, but typically require either high deposition temperatures or high temperature anneals (>600°C) to yield films with low resistivity and low fluorine contamination. MOCVD TaNx processes have been researched, but require temperatures in excess of 450°C to deposit films with resistivities below 1000µΩ·cm. Compatibility with proposed low-k dielectric materials, many of which are thermally fragile, dictates a thermal ceiling of 350-400°C.

Accordingly, low temperature (<350°C), non-fluorinated cvd processes for both wn and TaNx have been developed. The CVD WNx is deposited thermally using W(CO)6 and NH3 as the reactants. Both thermal and plasma-assisted techniques for CVD of TaNx films use TaBr5 as the metal source. The thermal process employs NH3 as the nitrogen source, and the plasma-assisted process uses a mixture of H2 and N2. This paper evaluates the films' material properties and copper diffusion barrier properties, demonstrating the feasibility of the materials and processes for advanced liner applications.
Basic Film Properties, Conformality, and Thermal Stability
Both types of films are deposited in dedicated, stand-alone 200mm wafer-capable tools. The systems are equipped with load-locks to prevent atmospheric contamination between depositions. Both the TaBr₅ and W(CO)₆, which are room temperature solids, are delivered by a commercially available pressure-based mass flow controller. Tables 1 and 2 list basic film properties for the CVD WNₓ and TaNₓ processes, respectively.

Table 1: Thermal CVD WNₓ properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (four point probe)</td>
<td>300-400μΩ-cm</td>
</tr>
<tr>
<td>Stoichiometry (AES)</td>
<td>W₂N phase</td>
</tr>
<tr>
<td>Crystal phase (XRD)</td>
<td>Amorphous or nanocrystalline</td>
</tr>
<tr>
<td>Contamination (XPS)</td>
<td>~3-5% each C and O</td>
</tr>
<tr>
<td>Step coverage (SEM, FIB-SEM, TEM)</td>
<td>&gt;70% (0.2μm, 6:1 aspect ratio structure)</td>
</tr>
<tr>
<td>Surface roughness (AFM)</td>
<td>&lt;5% of film thickness</td>
</tr>
</tbody>
</table>

Table 2: CVD and PACVD TaNₓ properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Thermal CVD</th>
<th>PACVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (four point probe)</td>
<td>2500μΩ-cm (as deposited)</td>
<td>~150μΩ-cm</td>
</tr>
<tr>
<td>Stoichiometry (AES)</td>
<td>TaN₁.₈±0.₁₂</td>
<td>TaN₁.₀±0.₀₂</td>
</tr>
<tr>
<td>Crystal phase (XRD)</td>
<td>Amorphous</td>
<td>Cubic (111)</td>
</tr>
<tr>
<td>Contamination (XPS)</td>
<td>&lt;0.5 at.% Br</td>
<td>&lt;2.5 at.% Br</td>
</tr>
<tr>
<td>Step coverage (SEM, FIB-SEM, TEM)</td>
<td>&gt;90% (0.13μm, 8:1 aspect ratio structure)</td>
<td>&gt;90% (0.2μm, 6:1 aspect ratio structure)</td>
</tr>
<tr>
<td>Surface roughness (AFM)</td>
<td>&lt;5% of film thickness</td>
<td>&lt;5% of film thickness</td>
</tr>
</tbody>
</table>

Both thermal and plasma-assisted CVD TaN processes yield films with low levels of Br contamination (<0.5 at. % for thermal CVD TaNₓ and ~2.5 at. % for PACVD TaNₓ). The bromine is thermally stable in the TaNₓ films up to at least 600°C. While the thermal CVD TaNₓ process offers an as-deposited amorphous structure, the plasma-assisted process yields films with lower resistivities due to its less nitrogen-rich stoichiometry. The amorphous microstructure of the TaNₓ films is thermally stable up to 600°C. Above this temperature, the film recrystallizes into a predominantly Ta₃N₅ phase.

At low deposition temperature (~200°C), the thermal WNₓ CVD process yields films with a consistent W₂N stoichiometry and an amorphous (or nanocrystalline) microstructure. When the deposition temperature increases, the films become more crystalline. Adhesion of these
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liners to SiO₂ is excellent, as measured by stud-pull testing.

The thermal stability of CVD W₂N samples was evaluated in a similar fashion: 500Å thick films do not recrystallize after 30 minute anneals at 650°C. For comparison, PVD W₂N films do recrystallize after such annealing.

The thermal CVD WNₓ process and both thermal and PACVD TaNₓ processes yield films with excellent conformality. Figure 1 is a cross-section FIB-SEM demonstrating the conformality of a ~500Å thick thermal CVD TaNₓ film.

Figure 1. FIB-SEM of a ~500Å thick thermal CVD TaNₓ film.
Step coverage in the 0.13µm structure is >90%, and is similar for PACVD TaNₓ and CVD WNₓ films.

Copper Integration and Diffusion Barrier Properties (back to top)
We studied the barrier and general integration properties of these liners, particularly the adhesion and crystallographic texture of copper seed layers. These liners provide a good surface for the subsequent growth of CVD copper films for seed and fill applications (Figure 2).

Figure 2. FIB-SEM of CVD copper fill over 0.18µm structures coated with CVD liner.

Thermal diffusion barrier testing on these liners used the following methodology:

- Liners are deposited on HF-dipped Si substrates. The thickness of the CVD WNₓ liners is 250Å, the thickness of the TaNₓ liners is 550Å;
- The liner/Si stacks are characterized by RBS, AES (or XPS), XRD, and four point probe, both as received and after annealing. The annealing conditions are 30 minutes at 450°C, 500°C, 550°C, 600°C, and 650°C, in ~300 torr ultra-high purity Ar;
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- 1000Å copper is sputtered on the as-received liners, and these stacks characterized with the same techniques as outlined above, again, both as received and after annealing with the method outlined above;
- The copper is stripped off using dilute nitric acid, and the films profiled by RBS for copper diffusion into the liner and/or Si substrate;
- The liner is stripped off using an appropriate chemistry, and a Secco etch performed.
- The films are then characterized for etch pits by SEM.

The 550Å thick thermal CVD TaNₓ and PVD TaNₓ liners appear to be stable up to 550°C, with both RBS and etch pit measurements indicating barrier failure above this temperature. Based on XPS, XRD, and RBS measurements, we attribute the barrier failure to thermally induced texture changes in the CVD TaNₓ films. Analogous testing is currently being performed on PACVD TaNₓ samples.

Similar copper diffusion barrier testing has been performed on 250Å thick CVD and PVD W₂N liners. As with the CVD TaNₓ samples, the tungsten-based CVD liners are stable after 30 minute anneals at 550°C.

Conclusions  (back to top)
CVD processes for the growth of WNₓ and TaNₓ liners have been developed. All processes are carried out at low temperature (200-275°C for CVD WNₓ, 350-425°C for CVD TaNₓ), allowing integration with low-k dielectric materials. The material properties and thermal stability of these materials make them attractive for advanced copper interconnect applications.

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Questions?
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