Intrinsic Properties and Barrier Behaviors of Thin Films of Sputter-Deposited Single-Layered and Alternately Layered Tantalum Nitrides (Ta$_2$N/TaN)

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This work employs X-ray diffraction, X-ray reflectivity, and transmission electron microscopy, along with electrical (sheet resistance and resistivity) and bending-beam stress analyses, to characterize the intrinsic properties and barrier behavior of 40 nm thick films of sputter-deposited single-layered Ta$_2$N, single-layered TaN, and alternately layered Ta$_2$N/TaN having various period thicknesses (l) from 4 to 40 nm. The thermal stability of each of these barriers in the temperature regime (500-900°C) is closely related to variations of intrinsic properties of the barriers, particularly microstructure and residual stress (σ). Failure of the barriers is explained in terms of a previously reported mass transport mechanism, which suggests that the free short-diffusion paths (grain boundaries) created by anneal-induced crystallization/grain growth in the single-layered Ta$_2$N and TaN barriers (σ = 3-5 GPa) are a key factor in deteriorating the diffusion barriers. Conversely, an adequately layered Ta$_2$N/TaN barrier with l down to approximately 5 nm is nearly free of residual stress and can maintain a very stable quasi-amorphous microstructure against annealing. Therefore, this quasi-superlattice novel design has the capability to further improve thermal stability and reliability of tantalum nitride diffusion barriers for copper metallization.

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Transmission electron microscopy (TEM) and X-ray diffractometry (XRD) conducted at a 30 keV copper Xe radiation at 20 mA were employed to identify the phase of the deposited films. Depth profiling secondary ion mass spectroscopy (SIMS) having a composition determination accuracy within ±2 atom %, as well as electron probe microanalysis (EPMA), were employed to determine the composition distributions of the single-layered films. These analyses indicated that the Ta$_2$N barrier layers can be deposited over a range of nitrogen concentrations that deviate slightly from stoichiometry, i.e., they range from approximately 33 to 38 atom %. All Ta$_2$N barriers examined here were identified as nitrogen oversaturated (~38 atom %), while TaN barriers had a stoichiometric composition. Conventional θ-2θ X-ray reflectivity measurements were recorded in a synchrotron radiation facility to evaluate the composition modulation of the Ta$_2$N/TaN multilayered barriers. Reflectivity analysis revealed that the multilayered Ta$_2$N/TaN barriers, with a period thickness (λ) of 6 nm or greater, have a well-defined composition modulation. Furthermore, following thermal cycling (25-400°C) of all the sample films, the magnitudes of the residual stress of the Ta$_2$N and TaN (single-layered) and Ta$_2$N/TaN multilayered barriers were also obtained via the bending-beam technique and Stoney’s equation to measure the curvatures of all of the sample films. To facilitate stress-induced curvature detection, all of the barrier films were deposited on 140 μm thick silicon (100) membranes. In addition, the microstructure, electrical properties and composition of the Ta$_2$N/TaN multilayered barriers were also examined by using XRD, TEM, resistivity measurement, and depth-profiling SIMS to compensate for the possible variations of the films’ intrinsic properties created by underlying sublayers. Table I displays the microstructure, composition, and values of electrical resistivity and residual stress of the as-deposited Ta$_2$N, TaN, and Ta$_2$N/TaN alternately layered barrier films that were examined herein.

The behavior of the 40 nm thick Ta$_2$N, and TaN, and Ta$_2$N/TaN multilayered films as barriers between copper and silicon was examined with samples on which a copper film 150 nm thick was deposited on the barrier films without breaking the vacuum. The performance of the Ta$_2$N/TaN multilayered barriers was optimized by broadly varying the period thickness from 4 to 40 nm. To directly compare the barriers, total thicknesses for all of the films were precisely controlled to be 40 nm. The as-deposited Si/barrier/Cu samples were annealed isothermally in a rapid thermal vacuum annealer (SINKU-REKO MILA-3000-P-N) for 5 min under argon ambient at temperatures ranging from 450 to 900°C (±1°C accuracy). A four-point probe system was used to measure the anneal-induced changes of sheet resistance on the Cu surfaces of the whole Si/barrier/Cu samples. By doing so, the degree of reaction and intermixing among the underlying Si substrate, capped Ta-N barrier and Cu overlayer can be estimated to evaluate the effectiveness of the various barriers. XRD was performed on these Si/barrier/Cu samples not only to characterize the change of the crystallinity of the barriers, but also to analyze the anneal-induced reaction products. Moreover, the failure behavior of the barriers was also analyzed by using a TEM (JEOL 120EX) to examine the plan-view and cross-sectional foils of postannealed Si/barrier/Cu samples.

### Results and Discussion

**Barrier behavior of single-layered Ta$_2$N.**—Figure 1 illustrates a typical set of XRD patterns for as-prepared Si/Ta$_2$N/Cu samples subjected to annealing at various temperatures ranging from 500 to 750°C for 5 min. The as-deposited (25°C) Ta$_2$N barriers contain a broad peak with a full width at half-maximum of ~5° (inset a of Fig. 1). Subsequently, after annealing at 600°C/5 min, this broad peak is converted into three sharp peaks with 20 centered at 33.98, 36.69, and 38.77° (inset b of Fig. 1). According to the XRD source data, the three sharp peaks correspond closely to the hexagonal Ta$_2$N (100), (002), and (101), respectively. This transition implies that the as-deposited Ta$_2$N barriers consist of an amorphous-like material, which tends to crystallize at temperatures ≥600°C. Meanwhile, the intensities of the copper (111) peaks increase after annealing at 500°C, which is probably induced by an annihilation of crystal defects and grain growth of the copper layer. However, as the annealing temperature exceeds the crystallization temperature (600°C), the intensities of the Cu peaks begin to gradually decrease owing to the formation of Cu$_3$Si (700°C). According to a cross-sectional TEM study, upon crystallization of the amorphous-like Ta$_2$N barriers into a coarse, equiaxed grain structure at 600°C, copper follows the free-short grain boundaries to speedily penetrate the crystallized barriers toward the underlying silicon substrates, which

### Table I. Intrinsic properties of various tantalum nitride diffusion barriers.

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Crystallinity</th>
<th>Resistivity (μΩ cm)</th>
<th>Nitrogen content (atom %)</th>
<th>Residual stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_2$N</td>
<td>Amorphous</td>
<td>250</td>
<td>38</td>
<td>−3.5</td>
</tr>
<tr>
<td>TaN</td>
<td>Nanocrystalline</td>
<td>270</td>
<td>50</td>
<td>−5.6</td>
</tr>
<tr>
<td>Ta$_2$N/TaN</td>
<td>Amorphous/nanocrystalline</td>
<td>265</td>
<td>38/50</td>
<td>−3.4 (λ=40 nm); −0.7 (λ=10 nm)</td>
</tr>
</tbody>
</table>

**Figure 1.** A series of XRD patterns for as-deposited (25°C) Si/Ta$_2$N (40 nm)/Cu samples after annealing for 5 min at fixed temperatures ranging from 500 to 750°C.
ultimately becomes completely consumed by silicon in form of Cu$_3$Si (700-750°C). TaSi$_2$ can be observed in 750°C-annealed samples (Fig. 1).

Diffuse rings dominate the electron diffraction patterns of amorphous-like Ta$_2$N thin foils, which are prepared by thinning as-deposited plan-view Si/Ta$_2$N/Cu samples using focused ion milling (inset of Fig. 2). The diffuse patterns correlate well with the broad XRD pattern, which is an insert of Fig. 1. Dark-field images (Fig. 2) recorded from the Ta$_2$N foils by placing an objective aperture on the first-order diffuse ring of the diffraction pattern (Fig. 2 inset), reveal that the film matrix possesses a weak contrast that is reminiscent of the amorphous structure. The mosaic spread within the matrix, as also evidenced from the faint Ta$_2$N rings, indicates that roughly 3 nm sized scattered Ta$_2$N crystallites are embedded in the amorphous matrix of the sputter deposited Ta$_2$N. Herein, the amorphous-structure dominated Ta$_2$N barriers are denoted as a-Ta$_2$N barriers. After annealing at 600°C/5 min, the diffuse rings within the diffraction pattern of the a-Ta$_2$N are transformed into several sharp rings (Fig. 3a inset). These rings are a part of crystalline hexagonal Ta$_2$N, which in turn is analogous to the XRD analysis results depicted in Fig. 1. Notably, the interplanar spacings of all of the crystalline phases examined in this work were determined accurately via a gold electron diffraction pattern, which calibrated the camera length of the TEM. Meanwhile, the bright-field image of Fig. 3a and related dark-field images reveal that the 40 nm thick a-Ta$_2$N barriers are transformed into polycrystalline hexagonal Ta$_2$N with coarse grain sizes that are typically 30 to 40 nm. Cross-sectional TEM micrographs (Fig. 3b) reveal that, after annealing an Si/a-Ta$_2$N/Cu at 600°C for 5 min, the speckle feature of the a-Ta$_2$N is transformed into a polycrystalline structure of columnar grains whose sizes approximate the thickness of the barrier. This transformation is also related to a transformation of the diffuse electron diffraction pattern into a sharp pattern resembling that inset in Fig. 3a. Combining the plan-view and cross-sectional TEM micrographs (Fig. 2 and 3) reveals that, upon 5 min annealing at temperatures $\geq$600°C, the a-Ta$_2$N barriers crystallize into equal-sized (30-40 nm) columnar structure upon annealing at 600°C. Owing to ability of the highly thermally stable Ta$_2$N barriers to retard copper diffusion, the Cu X-ray signal in Si/TaN/Cu after annealing broad peaks appear (inset a of Fig. 4). However, Fig. 4 verifies that the XRD patterns for the as-deposited (inset a) and any high temperature annealed (inset b) TaN barriers are both similarly broad. This finding implies that the Ta$_2$N barriers are more crystallization resistant than the a-Ta$_2$N barriers are, which crystallize into an equal-sized (30-40 nm) columnar structure upon annealing at 600°C.

Barrier behavior of single-layered TaN.——Figure 4 shows a series of XRD patterns for Si/TaN/Cu samples annealed isothermally at various temperatures ranging from 600 to 800°C for 5 min. It is difficult to identify the crystallinity and phase(s) of the as-deposited (25°C) TaN barrier using XRD because merely one or two

Figure 2. Plan-view TEM dark-field image and diffuse diffraction pattern (inset) indicate that the as-deposited Ta$_2$N barrier is dominated by the amorphous phase.

![Figure 2](image2.png)

Figure 3. Combining (a) plan-view and (b) cross-sectional TEM images and diffraction pattern (inset) reveals that the a-Ta$_2$N barrier is transformed into a structure of equiaxed coarse grains after annealing in Ar ambient at 600°C for 5 min.

![Figure 3](image3.png)

Figure 4. A series of XRD patterns for various as-deposited (25°C) Si/TaN (40 nm)/Cu samples after isothermal annealing for 5 min at temperatures ranging from 600 to 800°C.

![Figure 4](image4.png)
at 700°C for 5 min does not appear to fade whereas the intensities of the copper XRD peaks in Si/Ta$_2$N/Cu significantly decrease after the same annealing treatment (as indicated in a comparison of Fig. 1 and 4). Only annealing Si/TaN/Cu at 800°C/5 min causes the copper diffraction peaks to reduce significantly because of the formation of Cu$_3$Si.

Plan-view TEM bright-field and dark-field images clearly indicate that the as-deposited TaN barriers consist of nanocrystallites with grain sizes that are typically 3 nm (Fig. 5a). The finding that the sputter deposited TaN barriers possess a nanocrystalline structure correlates well with previous observations. After annealing at 750°C/5 min, the 3 nm sized TaN precipitates distribute evenly throughout dark-field images (Fig. 5b), and the TaN diffraction patterns sharpen (inset of Fig. 5b). This confirms that, upon annealing at 750°C, TaN barriers can still maintain an average grain size of roughly 3-5 nm. As mentioned earlier, the lack of free short routes such as fast diffusing columnar grain boundaries as those found in the crystallized Ta$_2$N barriers could explain why the nanocrystalline TaN barriers can more effectively block Cu than the a-Ta$_2$N barriers.

**Barrier behavior of alternately layered Ta$_2$N/TaN.**——The series of XRD patterns displayed in Fig. 6 indicates that the Si/Ta$_2$N-TaN (λ=10 nm)/Cu samples apparently differ from the Si/Ta$_2$N/Cu and Si/TaN/Cu samples to the extent that, after annealing at 800°C for 5 min, the Cu$_3$Si diffraction peaks cannot be observed; the copper (111) peak is still very intense. According to Fig. 6, the samples with the λ=10 nm compositionally modulated a-Ta$_2$N/TaN barriers annealed at 700°C (or above) for 5 min still exhibit a broad Ta$_2$N XRD peak (compare insets a and b of Fig. 6). This behavior differs significantly from that of the single-layered a-Ta$_2$N, whose broad peak is transformed into sharp Ta$_2$N peaks upon annealing at 600°C for 5 min (see Fig. 1). Transmission electron images and selected-area diffraction patterns (not shown) reveal that the as-deposited λ=10 nm a-Ta$_2$N/TaN barriers indeed contain a mixture of amorphous and nanocrystalline phases. Upon annealing at 750°C for 5 min, dark-field images and electron diffraction patterns indicate that the amorphous-like Ta$_2$N sublayers comprising the λ=10 nm composition-modulated films crystallize, but can hold their grains at sizes of typically ≤3 nm (refer to Fig. 7). We believe that the lengthening and complex grain boundaries presented by the Ta$_2$N/TaN...
randomly oriented and 3 nm sized grains can effectively retard the inward penetration of Cu. This retardation could explain why the copper XRD peaks for the Si/TaN/Cu and Si/Ta2N/TaN/Cu vanish entirely (Fig. 1 and 4). The value for each data point plotted in Fig. 8 is averaged from a minimum of five measurements, which displays a standard deviation within ±3%. Copper (1.7 μΩ cm) is a markedly better conducting material than Ta-N (~300 μΩ cm) and anneal-induced silicide phases (exceeding 50 μΩ cm). Thus, the rapid increase of sheet resistance at a given temperature (Tc) observed in Fig. 8 reflects the failure of the metalization layer owing to the formation of copper- and tantalum-silicides. Table II lists crystallization temperatures (Tc) of the various barrier layers and compares the single-layered a-Ta2N, single-layered TaN, and various alternately layered a-Ta2N/TaN barrier films. This comparison regards Tc and characteristic temperatures, which cause the disappearance of Cu X-ray signals (Tcu) and the formation of CuSi XRD peaks (Tsch) in the Si/barrier/Cu samples. The failure-related temperatures in Table II consistently confirm that effectiveness of the tantalum nitride barrier materials decreases in the following order: λ=10 nm Ta2N/TaN (Tc=800°C)>TaN(Tc=750°C)>λ=40nmTa2N/TaN(Tc=700°C)>a-Ta2N (Tc=650°C).

 **Barrier performance assessment.** Several investigations have postulated that crystal defects, including grain boundaries, dislocations, voids, free surfaces, and microcracks, are dominating routes for transporting a rapid diffusing species, which is chemically inert and thermodynamically stable with the barrier. As is well known, Ta2N and Cu are immiscible and chemically inert to one another. Thus, the free short grain boundaries in the crystallized Ta2N barriers (Fig. 3), which perpendicularly connect the top copper film and the underlying silicon substrate, could act as latent diffusion channels for Cu to quickly arrive at the silicon side. Our previous study demonstrated that the temperature transforming amorphous Ta2N barriers into equal-sized coarse columnar grains depends heavily on their interstitial nitrogen concentration. As Table II indicates, Ta2N barriers examined herein contain a higher nitrogen content (38 atom %), thus crystallizing into equiaxial coarse grains at higher temperatures (~600°C) and yielding a greater Tc of 650°C. Conversely, that study verified that a-Ta2N barriers that contain a reduced nitrogen content (33 atom %) possess a markedly reduced crystallization temperature of merely 450°C. This premature transformation forces the stoichiometric Ta2N (Ta62N38) barriers to yield a Tc of only ~550°C, which is approximately 100°C smaller than that of the Ta67N33 barriers. Apparently, the abundant grain boundaries in the crystalline Ta67N33 barriers accelerate the complete loss of Cu at a relatively low temperature (650°C) through the formation of Cu3Si. (See Table II for a summary of barrier performance between Ta67N33 and Ta62N38.) The short-diffusing paths can be virtually removed by adequately controlling the sputtering parameters (e.g., sputtering ambient, alloying element, substrate temperature, and ion bombardment) to deposit highly crystallization resistant nanocrystalline or amorphous-like barriers.

The experimental findings of this study verify that the 40 nm thick a-Ta2N/TaN alternately layered barriers with an optimum λ of 10 nm (potentially as low as ~5 nm) outperform the Ta2N and TaN single-layered barriers. However, XRD and TEM analyses, indicate that, after following annealing at 700°C/5 min, the a-Ta2N sublayer contained in the one period (λ = 40 nm) Ta2N/TaN barrier also sustains a crystallization/grain growth transition. This transition seriously degrades the one period Ta2N/TaN barrier (Table III), hence emphasizing the importance of adequate layering for the property-optimized Ta2N/TaN barrier to maintain a stable microstructure upon annealing. Optimization of the composition-modulated Ta2N/TaN barriers to outperform the Ta2N and TaN single-layered barriers was speculated. The innovative microstructure refining that this novel multilayered engineering approach achieves was determined as the answer. Nanocrystalline structure preservation within the Ta2N/TaN barriers inhibits the inward diffusion of copper effec-

**Table II.** A comparison of failure-related temperatures for the stacked samples using various barriers (40 nm thin) obtained from XRD and sheet resistance measurements.

<table>
<thead>
<tr>
<th>Characteristic temperature (°C)</th>
<th>Ta67N38</th>
<th>Ta67N33</th>
<th>TaN</th>
<th>Ta2N/TaN (λ = 40 nm)</th>
<th>Ta2N/TaN (λ = 10 nm)</th>
<th>Ta2N/TaN (Continuous)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tcu</td>
<td>750</td>
<td>650</td>
<td>800</td>
<td>750</td>
<td>900</td>
<td>-</td>
</tr>
<tr>
<td>Tsch</td>
<td>700</td>
<td>600</td>
<td>800</td>
<td>750</td>
<td>850</td>
<td>-</td>
</tr>
<tr>
<td>Tc</td>
<td>650</td>
<td>550</td>
<td>750</td>
<td>700</td>
<td>800</td>
<td>750</td>
</tr>
<tr>
<td>Te</td>
<td>600</td>
<td>450</td>
<td>-</td>
<td>700</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a Tcu is defined as where the intensity of Cu has decreased to a value of less than ~5% of the original intensity.
b This barrier was deposited by continuously varied nitrogen flow rates from 1.0 sccm (a-Ta2N) to 1.4 sccm (TaN).
tively by reducing diffusion short cuts substantially. The incorporated nitrogen that segregates to grain boundaries also could hinder grain growth and grain boundary diffusion. Moreover, the additional heterointerfaces between the Ta\textsubscript{2}N and TaN sublayers could disrupt the microstructure frequently, which possibly increase the number of copper trapping sites. Hence, diffusing copper can be blocked significantly.

X-ray reflectivity measurements demonstrated that, even at high angle regimes, X-rays scattered by the sharp electron density gradient at the interface regions in Ta\textsubscript{2}N/TaN multilayered films with $\lambda$ to $\sim$6 nm yield well-resolved Kiessig interference fringes.\textsuperscript{16} This finding implies that each individual sublayer of all of the Ta\textsubscript{2}N/TaN alternately layered films examined herein has a well-defined composition. In contrast, a-Ta\textsubscript{2}N/TaN barriers with a continuous composition gradient exhibit a performance approaching that of single-layered TaN barriers (see Table II). Moreover, as Table I lists, the magnitude of residual intrinsic stress for the $\lambda=10$ nm Ta\textsubscript{2}N/TaN films (0.7 GPa) is considerably smaller than that for the Ta\textsubscript{2}N and TaN single-layered films (3-5 GPa). This reduced stress, presumably permits the Ta\textsubscript{2}N/TaN films to occupy a lower free energy state, thus forcing the Ta\textsubscript{2}N sublayers to remain fully amorphous at the interface, which could be a factor that hinders grain growth of the Ta\textsubscript{2}N sublayers (each sublayer is only 5 nm thick). As equiaxed finer grains provide longer and more complex paths for Cu diffusion, the adequately layered Ta\textsubscript{2}N/TaN films have a greater ability to block the intermixing and reaction of copper and silicon, thus becoming superior diffusion barriers.

**Conclusion**

This work has investigated the thermal stability and barrier behavior of single-layered a-Ta\textsubscript{2}N, single-layered TaN, and alternately layered a-Ta\textsubscript{2}N/TaN films, as diffusion barriers between copper and silicon. Under the processing window defined herein, the thin Ta\textsubscript{2}N and TaN barriers can be deposited to have an amorphous-dominated and nanocrystalline structures, respectively. Results obtained from annealing Si/barrier (40 nm)/Cu samples at a high temperature regime (500–900°C) suggest that the single-layered a-Ta\textsubscript{2}N (and one-period Ta\textsubscript{2}N/TaN) barriers are deteriorated by the crystallization/grain growth of the amorphous Ta\textsubscript{2}N, probably aided by the enormous intrinsically frozen compressive stress ($\sim$3 GPa). Copper can easily follow grain diffusion mechanism to penetrate the crystallized Ta\textsubscript{2}N barriers and finally reacts with the underlying silicon, forming localized Cu\textsubscript{3}Si precipitates. However, after annealing at 750°C for 6 min, the TaN barriers still preserve the nanocrystalline structure to effectively eliminate the free short-circuit paths. Therefore, the TaN barriers outperform the a-Ta\textsubscript{2}N barriers. The property-optimized alternately layered Ta\textsubscript{2}N/TaN barriers can achieve a high chemical inertness by maintaining a nanocrystalline microstructure at any annealing temperatures to provide complex routes and trapping sites to frequently disrupt diffusion of copper. Therefore, the $\lambda=10$ nm alternately layered Ta\textsubscript{2}N/TaN barriers display the highest thermal stability by having the greatest failure temperature.

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