TaNx Thin Films Deposited Through Various Flow Ratios of N2/Ar for Copper Barrier Properties

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To optimize copper diffusion barriers, TaNx thin films for diffusion barriers were prepared by using radio frequency sputtering with various flow ratios of N2/Ar as the reactive gas. The component transformed from TaN to TaN4 as observed from deposition rates, and N/Ta ratios as N2/Ar flow ratios from 0.075 to 0.3. Furthermore, the structural transformations from body-centered cubic through face-centered cubic to nanocrystalline for TaNx thin film demonstrated under increase of N2/Ar flow rate, induced three-step stages for formation of TaNx thin film in Cu/TaNx/n+np+ diodes suggest that increasing flow ratio of N2/Ar from 0.075 to 0.3 enhanced the thermal stabilities from 450 to 550°C under leakage current conditions below 3 μA. The observation deduces that N2/Ar flow ratios dominated predominantly properties of TaNx films through crystal structure for barrier.

Copper metallization has been chosen for ultralarge scale integration due to its lower bulk resistivity (1.62 μΩ cm), better electromigration resistance, better stress-voiding resistance, and higher melting point (1084°C) than aluminum and aluminum alloys (Al–Si and Al–Si–Cu).1,2 Copper has emerged as an alternative interconnect and Al–Si–Cu melting point barriers.23–25 Due to the polycrystalline structure of Ta, grain boundary

argon. Structural and compositional changes in the layer stacks were monitored with glancing-angle X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) investigations. X-ray photoelectron spectroscopy (XPS) was used for monitoring concentration changes of all atoms. Although there is a growing interest in graded Ta–TaN barrier layer stacks, less is known about microstructure and thermal stability in Cu/TaNx/n+np+ diode systems. The Cu/TaNx/n+np+ diodes were fabricated for electrical measurements in leakage current to analyze the thermal stabilities of the TaNx diffusion barriers after rapid thermal anneal (RTA).

Experimental

For the investigations of the graded Ta–TaN diffusion barriers, 4 in. n-type thermally oxidized silicon wafers with [111] planes and 525 ± 25 μm thickness was utilized as the substrate. Thermal oxidation was carried out at a temperature of 1000°C for 120 min in oxygen ambient to grow a 140 nm SiO2 film. The wafers were cut into 1 × 1 cm squares, then a standard RCA clean was performed prior to loading the wafers into the loadlock. The TaNx thin films were deposited through radio frequency (rf) reactive sputtering by using N2/Ar as the mixed reactive gases under 300 W of rf power. The base pressure in the physical vapor deposition chamber was 3 × 10−5 Pa and 150 mm of the target-to-substrate distance. The N2/Ar flow ratios were varied at 0.075, 0.100, 0.125, 0.150, 0.175, 0.200, 0.225, and 0.300 for nitrogen content in the sputter chamber under 4.0 Pa of sputtering pressure. The Ta target was sputtered for 30 min to clean the surface, the so-called presputter process. The samples were sputtered by the Ta target prepared by the presputter process, and all TaNx thicknesses were around 150 nm. All samples were annealed under 10−7 Pa at 650°C for 3 h. Glancing-angle XRD measurements with an incidence angle of α = 2° were done at room temperature in parallel beam geometry with Cu Kα radiation (λ = 1.5418 nm) and thin-film equipment. The registered diffraction angle range was 2θ = 20°–95° with a step size of Δ2θ = 0.05° and a measuring time of 40 s per step. TEM investigations were carried out with a JEOL 1200EX microscope to identify the phase of the deposited films and crystal structure morphology. The deposition rates and roughness of the TaNx thin films were observed by cross-sectional TEM and atomic force microscopy (AFM), respectively. XPS was utilized to analyze the N and Ta content in the TaNx films and then the N/Ta ratio was estimated through these data.

The thermal failure property of the TaNx thin film was tested through the leakage current by Cu/TaNx/n+np+ diodes as shown in Fig. 1. The thicknesses of n+ n, and n layers in the n+np+ diode purchased from General Semiconductor were 20, 18, and 490 μm, respectively. The low-temperature oxide glass and medium-

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temperature oxide around 500, 800, and 700 nm thick were utilized to isolate each diode, respectively. The 25 nm thick TaN films were deposited as barriers on the n+np⁺ surface with 0.075, 0.175, and 0.3 of N₂/Ar flow ratios in the sputtering chamber. Then a copper film with 60 nm thickness was deposited on the TaN films by rf reactive sputtering with argon at 3 × 10⁻³ Pa. The as-deposited Cu/TaN/n+np⁺ diodes were annealed in a rapid thermal vacuum annealer for 10 min under argon ambient at temperatures ranging from 450 to 650°C (± 1°C accuracy) for RTA. The forward voltage was applied on the Cu/TaN/n+np⁺ diode, in which the negative voltage was connected with the copper electrode and the positive voltage was applied on the p⁺ layer electrode. The current-voltage (I-V) curves were utilized to monitor the current passing through the diode from p⁺ to the copper electrode, which was placed on the hotplate to increase the temperature from room temperature to 650°C as the forward voltage (−5 V) was applied on the diode. The leakage currents of the Cu/TaN/n+np⁺ diode were measured by a Sony Tektronix 370A operated at an applied potential of −5 V at temperatures from 450 to 650°C for evaluation of the thermal properties.

Results and Discussion

Deposition rate and the composite of the TaNx film.— Figure 2 shows the deposition rate of the TaN thin films and the N/Ta ratio estimated by XPS data in TaN thin films under various N₂/Ar flow ratios. The initial deposition rates of TaN thin films are approximated to 58 nm/min at N₂/Ar flow ratios from 0.075 to 0.125 and then decreased rapidly at the flow ratios from 0.15 to 0.2 as shown in Fig. 2. Additionally, the N/Ta ratios increased from 0.3 to 0.57 with flow ratios from 0.075 to 0.125. This observation suggests that the formation composite of Ta and Ta₂N thin films induced the N/Ta ratio below 0.5. The increasing N/Ta ratio ascribes diffusion of the N element into the vacancy around the Ta structure from the mixed gases of N₂ and Ar. The rapidly decreasing deposition rate as the N₂/Ar flow ratio increased from 0.15 to 0.2 indicates that the component of the thin film transformed from Ta₂N to TaN, corresponding to the N/Ta ratio increase from 0.55 to 1.15. This suggests that the vacancies around the Ta atom were occupied gradually by N atoms, which induced the transformation from Ta₂N to TaN, corresponding to the decrease of the deposition rate. The TaN thin film was formed gradually as the N₂/Ar flow ratio rose above 0.175, as shown in Fig. 2. The deposition ratio decreased gradually to approximately 22 nm/min as flow ratios rose from 0.2 to 0.3 due to the formation of TaN thin film. The interstitials around the TaN structure are occupied by the N element, causing the N/Ta ratio to increase to above 1 as the N₂/Ar flow ratios increased from 0.2 to 0.3. This observation suggests that the mixture composite of the Ta and TaN films with multiple phases were formed as the N₂/Ar flow ratio increased from 0.075 to 0.125, and the TaN films were formed as the N₂/Ar flow ratio rose from 0.175 to 0.2. The XPS spectra for Ta 4f in the TaN films deposited through various flow ratios of N₂/Ar are shown in Fig. 3. The binding energy of Ta 4f7/2 increased from 22.3 to 23.5 eV as the N₂/Ar flow ratio increased from 0.075 to 0.300. These Ta 4f7/2 peaks shifted to higher binding energies as the N₂/Ar flow ratios increased due to covalent shifting of Ta₂N to TaN in the thin films.

Structure and morphology of the TaNx film.— Figure 4 shows the XRD spectra obtained from the TaN thin films deposited with various flow ratios of N₂/Ar. The broad peak appears at angles of 38.7, which corresponds to the (101) reflections of hexagonal Ta₂N as N₂/Ar flow increases from 0.075 to 0.15. The broad peak is ascribed to the composite of Ta and Ta₂N in the bcc structure, which corresponds to a N/Ta ratio of 0.3–0.55. N/Ta ratio increased continuously as the flow ratio increased from 0.075 to 0.125, indicating that the thin films were composed mainly of Ta and Ta₂N. With the N₂/Ar flow ratio increasing, TaN film predominated in the films due to the obscure peaks for Ta₂N from the XRD spectra. The sharp peaks appear at diffraction angles of 35.2, 41.7, and 60.9, which correspond, respectively, to the (111), (200), and (220) reflections of TaN under fcc structure at a N₂/Ar flow ratio of 0.2. Therefore, the structures transformed from bcc (flow ratios of 0.075–0.125) to fcc (flow ratios of 0.175–0.200) polycrystalline structure. These peaks correspond to the disappearance of the fcc structure as the N₂/Ar flow ratio increased from 0.25 to 0.3, as deduced from the TaN structure transition from fcc to nanocrystalline. This observation suggests that the interstitials around the TaN structure are occupied by N, which impeded the formation of fcc structure in the TaN films as N₂/Ar flow ratios rose from 0.2 to 0.3, inducing the nanocrystalline formation of TaN films.
smaller radius (they contain only a few spots) can be seen, which correspond to interplanar spacings and interatomic distances as shown in Fig. 5a and b. Halo rings correspond to a little longer interatomic distance and spotted ones correspond to shorter ones than those of the polycrystalline structures. The TaN film demonstrates merely halo rings for TEM diffraction patterns due to the nanocrystalline structure, as shown in Fig. 5c. As the N2/Ar flow ratio was 0.075, the Ta2N thin film was formed into the bcc polycrystalline structure, verified by the ring pattern displayed in Fig. 5a, and the bright-field cross-sectional TEM images demonstrated the columnar-like structure. With increasing the N2/Ar flow ratio to 0.175, the Ta2N thin film transited to TaN thin film with fcc polycrystalline domain, verified by Fig. 5b and the bright-field cross-sectional TEM image, which indicates a preferred orientation of 111 corresponding to the XRD spectrum in Fig. 4e.33 As the N2/Ar flow ratio increased to 0.300, the TaN thin film with nanocrystalline structure demonstrates latticelike structure from the bright-field cross-sectional TEM image in Fig. 5c, corresponding to the XRD dispersive peaks in Fig. 4i. Bright-field plan-view TEM images of TaN thin films deposited through various N2/Ar flow ratios are shown in Fig. 6. The bright-field plan-view TEM images indicated that the grain sizes decreased from 22.6 to 11.8 to 6.9 nm as flow ratios increased from 0.075 to 0.175 to 0.300, respectively. Additionally, the grain size and roughness estimated from Fig. 6 and AFM images shown in Fig. 7 are summarized in Table I. Figure 7 shows AFM results which demonstrate the surface morphology with roughness data, distinguishing the surface morphology mainly. The AFM images in Fig. 7 with (a) 0.075, (b) 0.175, and (c) 0.300 of

**Figure 3.** XPS spectra for Ta4f in the TaN thin film deposited through a N2/Ar flow ratio of (a) 0.075, (b) 0.1, (c) 0.125, (d) 0.15, (e) 0.175, (f) 0.2, (g) 0.225, (h) 0.25, and (i) 0.3 after annealing at 600°C for 10 min.

**Figure 4.** XRD spectra of the TaN thin films deposited through a N2/Ar flow ratio of (a) 0.075, (b) 0.1, (c) 0.125, (d) 0.15, (e) 0.175, (f) 0.2, (g) 0.225, (h) 0.25, and (i) 0.3 after annealing at 600°C for 10 min.

**Figure 5.** Bright-field cross-sectional TEM images and diffraction patterns of TaN thin films deposited through N2/Ar flow ratios of (a) 0.075, (b) 0.175, and (c) 0.3 after annealing at 600°C for 10 min.
N$_2$/Ar flow ratios are similar images, showing the mixture structure under transformation from Ta$_2$N to TaN as the N$_2$/Ar flow ratio increases to about 0.175.

Grain densities calculated from these TEM images and resistivities of the TaN thin films were plotted as a function of N$_2$/Ar flow ratio in Fig. 8. Grain density approximated closed to a value as N$_2$/Ar flow ratio below 0.15 ascribes the bcc polycrystalline domain of Ta$_2$N films with 22.55 nm of grain size. As the N$_2$/Ar flow ratio rose above 0.175, the grain density increased rapidly due to the formation of fcc polycrystalline and nanocrystalline domain. We de-

Table I. The grain size and roughness estimated from AFM images with the various flow ratios.

<table>
<thead>
<tr>
<th>N$_2$/Ar reactive gas flow ratio</th>
<th>Grain size (nm)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.075</td>
<td>22.6</td>
<td>4.7</td>
</tr>
<tr>
<td>0.175</td>
<td>11.8</td>
<td>2.8</td>
</tr>
<tr>
<td>0.300</td>
<td>3.9</td>
<td>1.5</td>
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Figure 6. Bright-field plan-view TEM images of TaN thin films deposited through N$_2$/Ar flow ratios of (a) 0.075, (b) 0.175, and (c) 0.3 after annealing at 600°C for 10 min.

Figure 7. AFM images on TaN thin-film surfaces with (a) 0.075, (b) 0.175, and (c) 0.300 of N$_2$/Ar flow ratios after annealing at 600°C.
fined the midpoint of the flow ratio from 0.175 to 0.225 as a critical ratio, which represented the transitional point from bcc to fcc polycrystalline domain. The resistivity increased gradually with the increase of N2/Ar flow ratio from 0.075 to 0.15, and then rapidly increased as the N2/Ar flow ratio increased above 0.175–0.25, the so-called critical ratio. The fcc polycrystalline formation of TaN films caused the rapid increase of resistivity as the N2/Ar flow ratios rose above the critical ratio. This observation suggests that the resistivity of the TaN film corresponded to the grain density and the structure of the thin film. Increasing N content around the Ta atom varied the structure and the component of TaN film, inducing the increase of grain density. Therefore, the resistivity of TaN increased upon increase of N content, corresponding to the crystal structure. The TaN film resistivity of the crystal structure was concluded to be the following: bcc-Ta2N < fcc-TaN < nanocrystal-TaN.

Thermal property for leakage current.— The leakage current for thermal treatment was measured under −5 V of forward voltage for Cu/TaN1.13/n+np+ diode at room temperature, 500°C, 550°C, and 600°C, respectively, to analyze the thermal stability as shown in Fig. 9. At room temperature, the electron was obstructed by TaN film, causing the leakage current to be −0.5 μA as −5 V of the forward voltage was applied on the diode. With a temperature increase to 500°C, the leakage current increased slightly to −1.5 μA at −5 V, as shown in Fig. 9b, suggesting that the copper atom was slightly diffused through barrier in the Cu/TaN1.13 (25 nm)/n+np+ diode. The leakage current increased to −14 μA at −5 V, as shown in Fig. 9c, due to the diffusion of Cu through the TaN barrier layer into the n+np+ diode as temperature closed to 550°C. The leakage current increased to −1140 μA at the applied voltage, referring to the collapse of the TaN barrier layer as temperature approached 600°C, as shown in Fig. 9d. The observation suggests that copper atoms diffused slightly into the barrier layer at around 500°C, which caused the leakage current increase. The thermal capability for the TaN diffusion barrier was defined as the highest thermal stability under leakage current less than 3 μA with increasing temperature.23 Table II summarizes the highest thermal stability temperatures of Cu/TaNx/n+np+ samples (x = 0.31, 1.13, and 1.42) under 0.075, 0.175, and 0.300 of N2/Ar flow ratio. The highest thermal stability for the TaNx diffusion barriers increased with the N/Ta ratio due to the increasing electron charge cloud density from the N element, which resisted the copper diffusion through TaNx film through repulsive force.31 Thus, the TaN film demonstrated the optimum thermal property as the x value closed to 1.42.

![Figure 8. Grain densities and resistivities of TaNx thin films deposited through the various N2/Ar flow ratios after annealing at 600°C for 10 min.]()
The TaN thin films deposited through various flow ratios of N$_2$/Ar demonstrated structural transition from bcc through fcc to nanocrystalline, corresponding to deposition rate, N/Ta ratio, and grain density of TaN films. The results suggest that the N$_2$/Ar mixed gases dominated the formation of TaN films in various structures and composition. Furthermore, the TaN films were mainly composed of Ta$_2$N and TaN films in various structures by increasing the N$_2$/Ar flow ratio from 0.075 to 0.3, observed by the deposition rate in three step stages. The thermal stabilities of TaN films were dependent predominantly on their crystal structure and composite. Increasing N/Ta ratios enhanced the thermal stabilities for the Cu/TaN/n+np$^*$ diode structure to approach the optimum thermal property for copper barriers.

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