

# Plasma-enhanced atomic layer deposition of tantalum nitride thin films using tertiary-amylimido-tris(dimethylamido)tantalum and hydrogen plasma

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**Abstract** Plasma-enhanced atomic layer deposition (PEALD) of tantalum nitride (TaN) thin films was investigated at a growth temperature of 230 °C using an alternating supply of tertiary-amylimido-tris(dimethylamido)tantalum (TAIMATA, Ta[NC(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>][N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>) and hydrogen (H<sub>2</sub>) plasma. As the H<sub>2</sub> plasma power increased from 75 to 175 W, the electrical resistivity of the films was improved from 1900 to 680 μΩ·cm, mainly due to the improved crystallinity. Moreover, the preferred orientation ratio between TaN (200) and TaN (111) planes also abruptly increased from 0.8 to 2.8 with increasing the H<sub>2</sub> plasma power. This preferred orientation change of the films from (111) to (200) improves the adhesion properties between Cu and TaN, while the Cu diffusion barrier performance was not significantly affected.

**Keywords** Tantalum nitride thin films · Plasma-enhanced atomic layer deposition · Preferred orientation · Microstructure · Copper diffusion barrier

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## 1 Introduction

Copper (Cu) is widely used as a low-resistive interconnection metal in current microelectronic devices [1, 2]. For the use of Cu as an interconnection metal, a diffusion barrier layer is generally prepared between Si-containing low-k dielectrics and Cu to prevent the degradation of microelectronic devices caused by the diffusion of Cu [1–4]. For this application, atomic layer deposition (ALD) [5], and plasma-enhanced ALD (PEALD) [6–8] of tantalum nitride (TaN) thin films have been extensively investigated as an effective method for preventing Cu diffusion because TaN has a high thermal stability and low-reactivity with Cu [6–8], and the inherent merits of ALD or PEALD method, such as good step coverage over a large area, low growth temperatures, and precise thickness controllability [5–8], make them a very fascinating method for the fabrication of Cu diffusion barrier layer. In the microelectronic industry, TaN thin films are used in a stacked structure, where a Ta thin film is prepared on the TaN to increase the adhesion strength between Cu and TaN [3]. In the Ta/TaN stacked structure, however, the growth of an additional Cu seed layer is mandatory, because the electrical conductivity of Ta is not sufficient to ensure successful bottom-up Cu electro-filling [4–9]. Anticipated device shrinkage presents technical challenges for the construction of this complex structure (Cu seed/Ta adhesion layer/TaN diffusion barrier). Future interconnections will be difficult to construct with these structures, due to the smaller size requirements [4, 10]. Meanwhile, ruthenium (Ru) has received much attention as a potential Cu direct-platable diffusion barrier, due to its low electrical resistivity, its immiscibility with Cu, and its good adhesion properties with the Cu layer [4, 9–11]. However, its poor adhesion properties with Si, SiO<sub>2</sub>, and Si-containing low-k dielectrics, as well as its insufficient performance as a diffusion barrier, prevent fabrication of a Cu diffusion barrier made from Ru alone

[4, 10, 11]. Accordingly, a Ru/TaN structure has recently been suggested as a potential diffusion barrier structure [11, 12]; this structure does not require an additional Cu seed layer, as opposed to the conventional Ta/TaN structure. Thus, TaN is still regarded as a good material for Cu diffusion barrier layers, regardless of the changes in the stacking structure.

Up to now, various metal-organic [5, 6] and halides [7, 8] precursors have been studied for ALD or PEALD fabrication of TaN thin films. The most studies has been focused on the control of Ta:N ratio of the TaN films to exclude the formation of highly resistive Ta<sub>3</sub>N<sub>5</sub> phase. By a careful control of various deposition parameters, a stoichiometric TaN thin films were able to be successfully obtained. Nevertheless, extensive research efforts continue to push toward further improvement of the electrical and physical properties of TaN thin films via newly developed precursors and optimized ALD/PEALD-TaN processes.

In this study, we investigated the properties of TaN thin films via PEALD using tertiary-amyrimido-tris(dimethylamido) tantalum (TAIMATA, Ta[NC(CH<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>][N(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>) and hydrogen (H<sub>2</sub>) plasma. An early study of PEALD-TaN using TAIMATA [13] was performed by Hong et al. (2004); however, this study did not examine the effect of the growth parameters on the physical and electrical properties of PEALD-TaN. Also, PEALD of TaN using TAIMATA was investigated by our group [14], where the growth behavior of TaN depending on the TAIMATA and H<sub>2</sub> plasma time was mainly investigated. However, the adhesion properties between Cu and TaN as well as Cu diffusion barrier performance depending on the growth parameters of PEALD-TaN was not systemically investigated yet. Herein, therefore, we describe our in-depth investigation of the effect of H<sub>2</sub> plasma power on physical and electrical properties of TaN films fabricated using PEALD, with emphasis on the importance of preferred orientation of TaN thin films for the desired diffusion barrier film properties. The adhesion properties as well as Cu diffusion barrier performance depending on the H<sub>2</sub> plasma power were also carefully investigated.

## 2 Experiment

TaN films were deposited on 100-nm-thick SiO<sub>2</sub>/Si substrates by PEALD at a growth temperature of 230 °C using an alternating supply of TAIMATA and H<sub>2</sub> plasma. The deposition pressure was kept at 3 Torr. TAIMATA was contained in a bubbler, which was heated to 60 °C and delivered to the reactor via an argon (Ar) carrier gas at a flow rate of 50 sccm. The feeding line was heated to 95 °C to prevent condensation of the TAIMATA precursor. During deposition, Ar gas was continuously supplied to the reactor at 100 sccm, and an additional 50 sccm of Ar gas was introduced with each purge pulse. One deposition cycle of PEALD-TaN consisted of four steps:

(i) exposure of TAIMATA; (ii) purge pulse with 50 sccm of Ar; (iii) H<sub>2</sub> plasma exposure; and (iv) another purge with 50 sccm of Ar. During the H<sub>2</sub> plasma pulse, the radio-frequency plasma was operated in the range of 75 to 175 W with 50 sccm of H<sub>2</sub> gas. This cycle was repeated as many times as necessary to obtain the desired film thickness.

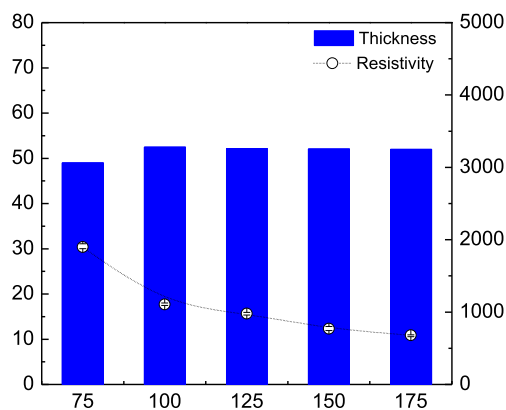
The film thickness was analyzed by field-emission scanning electron microscopy (FESEM), and the film composition was analyzed by 9.0 MeV He<sup>2+</sup> Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES). The sheet resistance was measured using a four-point probe, and the film resistivity was calculated from the sheet resistance and the measured film thickness. The microstructures of the films were studied by X-ray diffraction (XRD) with Cu-K $\alpha$  radiation at  $\lambda = 0.15405$  nm. Two modes of XRD were used: a glancing angle mode with a fixed incident angle of  $\theta = 3^\circ$  and a  $\theta$ - $2\theta$  coupled mode. A peel-off test [4] using 3 M scotch tape was performed to evaluate the relative adhesion strength between TaN thin films and 500 nm-thick Cu films prepared by MOCVD. To quantitatively analyze the adhesion property, square grids were made on the 2 cm by 2 cm square samples with 2-mm intervals. The outcome of the test was evaluated by counting the number of Cu square grids that had peeled off. Finally, Cu diffusion barrier properties were evaluated by measuring the electrical resistivity of Cu (100 nm)/TaN (5 nm)/Si samples after rapid thermal annealing (RTA) for 10 min in Ar ambient. For the evaluation of Cu diffusion barrier properties, 100-nm-thick Cu films were deposited by a dc sputtering system.

## 3 Results and discussion

To find an efficient reducing agent for TAIMATA, six reactants were investigated, as shown in the Table 1. After repeating 400 deposition cycles for each of the reactants, the film growth was examined by FESEM. To ensure a sufficient

**Table 1** Effect of the reactant on the deposition of TaN thin films by PEALD at a growth temperature of 230 °C and pressure of 3 Torr. To ensure sufficient reaction time, the pulse times of the TAIMATA and the reactant (or plasma) were fixed at 15 and 20 s respectively. The flow rate of each reactant gas was fixed at 50 sccm. When the plasma was used, the plasma power was maintained at 100 W. The other conditions were as described in the experimental section of the paper

Reactant	Film growth	Resistivity	Crystal structure
H <sub>2</sub> gas	No film growth.	-	-
NH <sub>3</sub> gas	○	$\sim 10^{10}$ $\mu\Omega\cdot\text{cm}$	Ta <sub>3</sub> N <sub>5</sub> + TaN
NH <sub>3</sub> plasma	○	$\sim 10^8$ $\mu\Omega\cdot\text{cm}$	Ta <sub>3</sub> N <sub>5</sub> + TaN
Ar plasma	No film growth.	-	-
N <sub>2</sub> plasma	○	$10^5 \sim 10^7$ $\mu\Omega\cdot\text{cm}$	Ta <sub>3</sub> N <sub>5</sub> + TaN
H <sub>2</sub> plasma	○	$\sim 1000$ $\mu\Omega\cdot\text{cm}$	Cubic-TaN



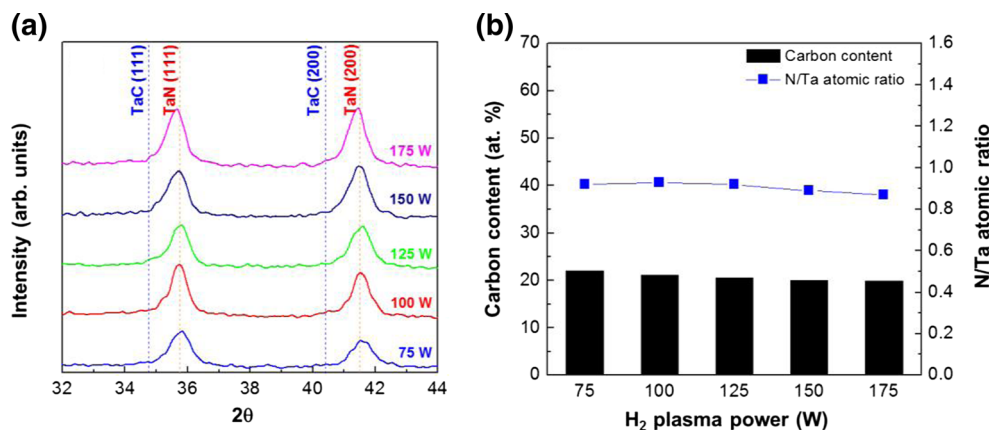
**Fig. 1** Dependence of the film thickness (nm) and corresponding electrical resistivity on the H<sub>2</sub> plasma power. The pulse times for TAIMATA and H<sub>2</sub> plasma were kept at 5 and 20 s, respectively. The film thickness and electrical resistivity was measured after 400 PEALD cycles

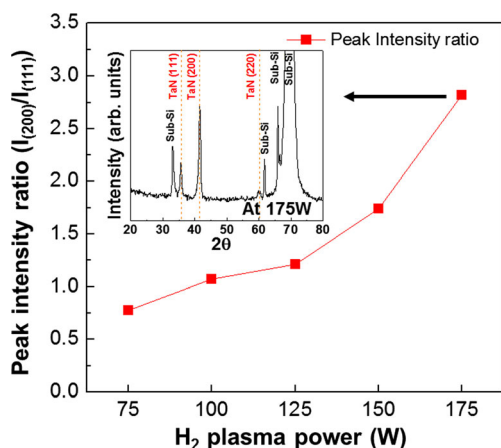
supply of TAIMATA and reactant during the deposition, the pulse times of TAIMATA and reactant were fixed at 15 and 20 s, respectively. The electrical resistivity and crystal structure of the films were analyzed. From this preliminary experiment, it was revealed that the use of H<sub>2</sub> gas and Ar plasma resulted in no film growth. Meanwhile, NH<sub>3</sub> gas, NH<sub>3</sub> plasma, N<sub>2</sub> plasma, and H<sub>2</sub> plasma resulted in the growth of films. However, the films grown with reducing agents containing nitrogen, such as NH<sub>3</sub> gas, NH<sub>3</sub> plasma, and N<sub>2</sub> plasma, exhibited high electrical resistivity; this indicated the formation of highly resistive Ta<sub>3</sub>N<sub>5</sub> phases, which was confirmed by XRD analysis (data not shown here). Previous reports have described similar behavior, where nitrogen-containing gas or plasma was used to deposit TaN thin films [6, 8]. It is well-known that Ta<sub>3</sub>N<sub>5</sub> phases are thermodynamically stable compared with TaN and that the control of nitrogen is very important for preparing stoichiometric TaN thin films. Because the use of H<sub>2</sub> plasma resulted in moderate electrical resistivity as well as cubic-TaN phases, we investigated the effect of the use of H<sub>2</sub> plasma on the microstructural evolution, electrical properties, and composition of the films. In our previous study [14], it was revealed that the saturation growth rate of

0.132 nm/cycle was obtained at a H<sub>2</sub> plasma power of 100 W when the pulse time of the TAIMATA and H<sub>2</sub> plasma were longer than 4 and 20 s, respectively. Although the growth rate was saturated at longer H<sub>2</sub> plasma pulse times of 20 s, the electrical resistivity of the TaN thin films further decreased from 1000 to 760 μΩ·cm when the H<sub>2</sub> plasma pulse time increased from 20 to 30 s, respectively. It was due to the improved crystallinity, the reduced N/Ta atomic ratio, and the reduced carbon contents of the TaN films. The formation of low resistive TaC phase at longer H<sub>2</sub> plasma pulse time also contributed to the lower resistivity of the TaN thin films, while the hydrocarbons were observed at short H<sub>2</sub> plasma pulse time than 20 s. The existence of hydrocarbon within the films also influenced the peak position shift from the ideal cubic-TaN peak positions to the higher angles. From this early studies, it was revealed that a sufficient H<sub>2</sub> plasma time is very important for improving the electrical resistivity of the TaN films.

First, the effect of the H<sub>2</sub> plasma power on the thickness of the film and the electrical resistivity after repeating 400 PEALD cycles was investigated. The durations of the TAIMATA and H<sub>2</sub> plasma pulses were held constant at 5 and 20 s, respectively, which is decided from our early study in order to ensure the saturated film growth. As shown in Fig. 1, the thicknesses of the films increased slightly from 49 to 52 nm as the H<sub>2</sub> plasma power increased from 75 to 100 W. As the H<sub>2</sub> plasma power increased beyond 100 W, the film exhibited a similar thickness of ~52 nm. Meanwhile, the electrical resistivity gradually decreased from 1900 to 680 μΩ·cm as the plasma power increased from 75 to 175 W. Although there were small changes (about 3 nm) in the film thickness, depending on the H<sub>2</sub> plasma power, these were not sufficient to explain the observed variation in the electrical resistivity. Therefore, we investigated the variation in crystalline structure and chemical composition using glancing angle XRD and AES. In contrast to the effect of varying the H<sub>2</sub> plasma pulse duration, any peak shift to higher or lower angles was not observed, as shown in Fig. 2(a). On the other hand, the crystallinity of the film, especially in the (200) orientation, improved with increasing H<sub>2</sub> plasma power. Moreover, AES

**Fig. 2** (a) Glancing angle XRD patterns of TaN thin films with varying H<sub>2</sub> plasma power. (b) Carbon contents and N/Ta atomic ratio of TaN thin films with varying H<sub>2</sub> plasma power. For (a) and (b), the pulse times of the TAIMATA and H<sub>2</sub> plasma were fixed at 5 and 20 s, respectively





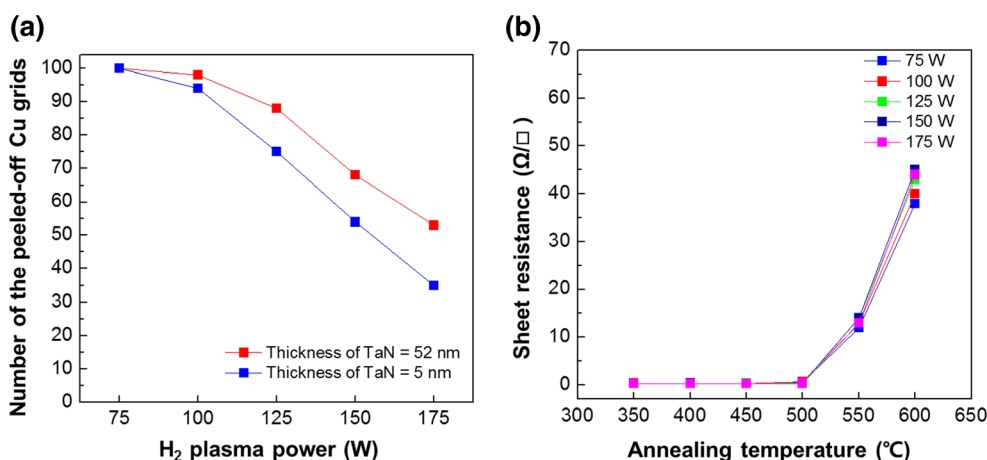
**Fig. 3** Peak intensity ratios of  $I_{(200)}$  and  $I_{(111)}$  depending on the  $H_2$  plasma power. For  $H_2$  plasma power between 50 to 150 W, the peak intensities of TaN (111) and TaN (200) were calculated from the  $\theta$ - $2\theta$  coupled XRD data of ref. 14. And, the inset image shows the  $\theta$ - $2\theta$  coupled XRD data for TaN thin films deposited at 175 W

analysis indicated that the carbon content and the N/Ta atomic ratio of thin TaN films decreased slightly when the  $H_2$  plasma power increased; however, these changes were not significant. From these results, it can be concluded that the improved degree of crystallinity is the most important contributing factor to the improved electrical resistivity of TaN thin films. This improvement in crystalline structure is achieved by increasing the  $H_2$  plasma power, which provides higher energy to the surfaces. The chemical variation of the film can also contribute to the improved electrical resistivity; however, its effect is less important. This conclusion is supported by the fact that no peak shift was observed and that the film thickness and chemical compositions varied only slightly.

We then quantitatively investigated the effect of the  $H_2$  plasma power on the preferred orientation of the TaN thin

films by XRD using the  $\theta$ - $2\theta$  coupled mode. In Fig. 3, the ratio of the TaN (200) peak intensity per TaN (111) peak intensity,  $I_{(200)}/I_{(111)}$ , was calculated from the previous  $\theta$ - $2\theta$  coupled XRD data for 75 and 150 W [14] and for 175 W (inset image). The preferred orientation ratio ( $I_{(200)}/I_{(111)}$ ) of the (200) planes continuously increased from 0.8 to 2.8 as the  $H_2$  plasma power increased from 75 to 175 W. According to a previous report for PVD-TaN [15, 16], similar changes in the preferred orientation from the (111) plane to the (200) plane were observed by increasing the growth temperature; the transition from the (111) preferred orientation to the (200) preferred orientation occurred at 400 °C. They explained that the (200) orientation of TaN is strongly preferred to minimize the surface energy of the films when sufficient thermal energy is supplied. As with the high growth temperature, higher  $H_2$  plasma power can provide more energy to the surface during deposition. Thus, the preferred orientation change from (111) to (200) can occur with PEALD at a lower growth temperature of 230 °C.

The effects of the preferred orientation change of TaN thin films resulted from the  $H_2$  plasma power on the adhesion properties and Cu diffusion barrier performance was investigated in detail. First, the adhesion properties between TaN and Cu depending on the  $H_2$  plasma power was quantitatively evaluated by a peel-off test, as shown in Fig. 4(a). The peel-off test was performed using 500-nm-thick MOCVD Cu/TaN thin films/ $SiO_2$ /Si samples. Two different film thicknesses (52 and 5 nm) of TaN were used to evaluate the influence of the film thicknesses. For a 52-nm-thick TaN films, the Cu film readily peeled off of the TaN surfaces when plasma power was lower than 100 W. However, the adhesion strength gradually improved as the preferred orientation ratio of the (200) orientation of TaN thin films increased with increasing  $H_2$  plasma power. Considering the interplanar distance of the TaN (200)



**Fig. 4** (a) Peel-off test results for 500-nm-thick Cu/TaN/ $SiO_2$ /Si samples. The thickness of TaN thin films was 5 and 52 nm, respectively. The number of peeled-off Cu grids was counted after the peel-off test. This test was performed five times; the average values are

presented in this figure. (b) Variation of the sheet resistance of 100-nm-thick Cu/5-nm-thick TaN/Si samples as a function of annealing temperatures. The annealing was performed for 10 min in Ar ambient using a rapid thermal annealing (RTA) system



plane ( $d_{200} = 0.2169$  nm), TaN (111) plane ( $d_{111} = 0.2504$  nm), and the Cu (111) plane ( $d_{111} = 0.2088$  nm), a smaller mismatch between TaN (200) and Cu (111) in the interplanar distance can improve the adhesion strength [17]. Also, the further improvement of adhesion between Cu and TaN was observed when the thickness of TaN thin films was reduced to 5 nm, while showing a similar trend with increasing the  $H_2$  plasma power. In general, the adhesion of the film is deteriorated by the increased film thickness due to the increased residual stress of the film [18]. Therefore, it was thought that the improved adhesion with a 5-nm-thick TaN thin films may be due to the reduced residual stress. Moreover, it is worthy to mention that further improvements to the adhesion properties between Cu and TaN may be achieved by further increasing the  $H_2$  plasma power, as this would induce a stronger preferred orientation along the (200) orientation of the TaN thin films.

Finally, the Cu diffusion barrier properties of 5-nm-thick TaN thin films depending on the  $H_2$  plasma power was investigated. Fig 4(b) shows the sheet resistance changes of the Cu/TaN/Si stacked structures after annealing in ambient of Ar for 10 min as a function of annealing temperature. For this, 5-nm-thick TaN thin films were used as a Cu diffusion barrier layer. Although the preferred orientation of TaN thin film was varied with  $H_2$  plasma power, the abrupt increase in the sheet resistance occurred after annealing at 550 °C for all the samples. According to the previous report [19], it was explained that Cu diffusion barrier property of CVD-TaN was inferior to that of PVD-TaN due to its loosely packed (200) preferred orientation. However, in that case, the difference in the impurities between CVD-TaN and PVD-TaN was not taken into consideration, despite the carbon and oxygen impurities in the CVD-TaN was much higher than those in the PVD-TaN. In our case, the difference in the impurity concentration was not high, while the preferred orientation of the films significantly changed. Therefore, it seems that the difference in the preferred orientation did not exhibit a visible difference in the Cu diffusion barrier property, probably because the PEALD-TaN still remained as a polycrystalline structure.

## 4 Conclusion

We investigated PEALD of TaN thin films using TAIMATA and  $H_2$  plasma. The  $H_2$  plasma power affected to the electrical properties, crystallinity, and chemical composition of the TaN thin films. Particularly, the preferred orientation of the films

depended strongly on the  $H_2$  plasma power. As the  $H_2$  plasma power increased, the preferred orientation of the TaN thin films changed from (111) to (200). With a smaller mismatch between the TaN (200) plane and the Cu (111) plane, the adhesion strength between TaN and Cu layers was improved. Moreover, the Cu diffusion barrier properties were not significantly affected by the change in the preferred orientation.

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