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# Thermal Stability of TaN-Based Thin Layers for Cu Metallization

Julien Nazon,\* Marie-Hélène Berger, Joël Sarradin, Jean-Claude Tedenac, Nicole Fréty

The diffusion of Cu through TaN-based thin layers into a Si substrate has been studied. The barrier efficiency of TaN/Ta/TaN multilayer barrier of 50 nm:50 nm:50 nm in thickness has been investigated and is compared with that of TaN single layers. Thermal stabilities of these TaN-based thin layers were determined from glancing incidence angle X-ray diffraction and transmission electron microscopy, conducted in the temperature range of 773–973 K. The TaN/Ta/TaN barrier appeared to be more efficient than the TaN single layer in preventing Cu diffusion.

## Introduction

With the increase in the integration density and the shrinkage of the interconnection design rules, new metallization scheme using copper has been suggested as a suitable candidate for metallization material in recent years to overcome high resistivity and low electromigration resistance of the conventional aluminum and/or aluminum alloys.<sup>[1,2]</sup> The major problem posed by Cu metallization is its high diffusivity in silicon, silicon dioxides, and other dielectrics used in integrated circuits under the high temperatures encountered in device fabrication. The interaction copper with silicon at deposition temperatures, even after annealing at 200 °C, results in degradation of the electrical integrity of the microelectronic devices by formation of copper silicide precipitates.<sup>[3]</sup> Thus, it is necessary to develop an effective barrier thin layer between Cu and Si or SiO<sub>2</sub> to prevent the diffusion of Cu.

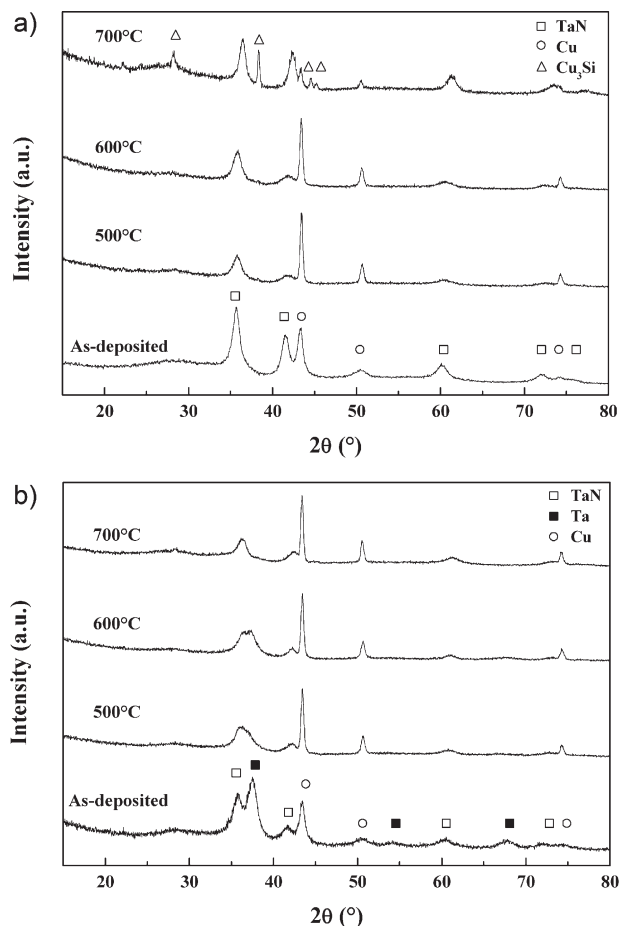
This barrier must be unreactive toward both copper and silicon and should exhibit a good adhesion to both copper

and silicon. Furthermore, the resistivity should be less than 1 000  $\mu\Omega \cdot \text{cm}$  to maintain an excellent electrical conductivity between the copper and silicon features.<sup>[4]</sup> That is the reason why tantalum nitride (TaN) films have received considerable interest in recent years as an efficient material for diffusion barrier because of their inherent properties, including high thermal stability and good conductivity.<sup>[5,6]</sup>

Since thin films can undergo diffusion processes during the fabrication of integrated circuits, which results in degradation of their performances, the understanding of diffusion mechanisms in thin films is of a great interest for controlling the quality of microelectronic devices, in terms of both efficiency and stability. For this reason, the efficiency of TaN thin film barrier against copper diffusion into silicon substrate has been investigated by many researchers.<sup>[5,7–10]</sup> It is reported that the thermal stability of TaN thin films depends on the diffusion barrier microstructure. Due to the polycrystalline structure of TaN thin films, the diffusion mechanism in the TaN barrier is controlled by grain boundary diffusion. The grain boundaries offer diffusion paths by which copper migrate to the silicon substrate.<sup>[5,7–9]</sup> However, from the reactive sputtering process, which is commonly used to deposit TaN thin films, TaN layers are grown with a characteristic columnar structure perpendicular to the substrate, associated with intercolumnar voids.<sup>[11,12]</sup> The diffusion mechanism may be assumed to be the copper migration through the TaN intercolumnar voids, which may be considered as the major diffusion paths.<sup>[11]</sup>

That is the reason why, in this work, multilayer barriers are sputter deposited in order to modify the copper

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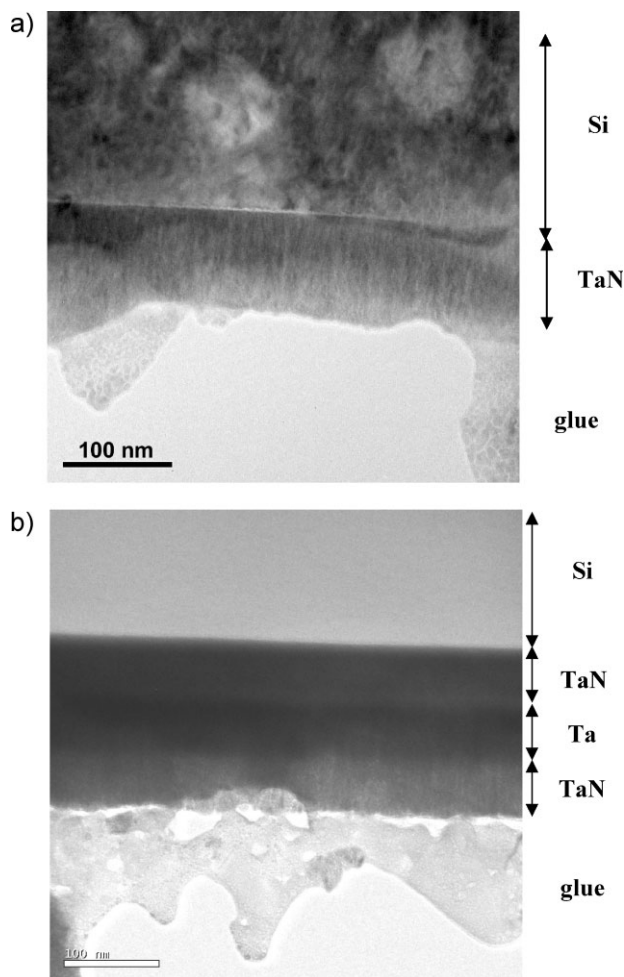


**Figure 1.** Glancing angle XRD patterns of the as-deposited samples and annealed at different temperatures  $T_{\text{annealing}}$  for a duration of  $t_{\text{annealing}} = 30$  min (a) Si/TaN/Cu (b) Si/TaN/Ta/TaN/Cu.

diffusion paths to improve the performance of the barrier layers. The aim of this work is to study the thermal stability of novel thin multilayered TaN/Ta/TaN diffusion barrier for Cu metallization and is compared with that of TaN single layer. This work is based on the observation of the interfacial reaction between Cu and Si in the 773–973 K temperature range and related to the microstructure of thin films. TaN and TaN/Ta/TaN barriers are deposited by radio-frequency reactive sputtering and annealed for 30 min from 500 to 700 °C. Structural changes and diffusion mechanisms are investigated by microstructural analysis.

## Experimental Part

TaN and TaN/Ta/TaN diffusion barriers were deposited onto n-type (111) orientated Si wafers with a resistivity of 15–18  $\Omega \cdot \text{cm}$  by radio-frequency (r.f.) sputtering. Prior to deposition, the native oxide formed at the surface of the silicon substrates was removed



**Figure 2.** TEM cross-sections of the as-deposited layers (a) TaN and (b) TaN/Ta/TaN.

using diluted HF chemical etching and the target was cleaned by pre-sputtering in Ar plasma. Ta and TaN thin films were sputtered under Ar and Ar–N<sub>2</sub> plasma, respectively, using a tantalum target (Johnson Matthey 2 in diameter) as previously described. The Ar gas pressure and the sputtering power were 6.5 Pa and 90 W, respectively. A 2% N<sub>2</sub> gas partial pressure allowed stoichiometric TaN to form. The TaN and TaN/Ta/TaN barriers were 150 nm thick, each layer thickness being of 50 nm for the multilayer one. A 100 nm thick Cu thin film was deposited on top of these barrier layers using a copper target (Johnson Matthey 2 in diameter) under an Ar plasma. The Ar gas pressure and the sputtering power were 13 Pa and 90 W, respectively.

In order to investigate the thermal stability of TaN and TaN/Ta/TaN diffusion barriers, the as-deposited samples with Si/TaN/Cu and Si/TaN/Ta/TaN/Cu structures were annealed in a vacuum of  $2.10^{-4}$  Pa in the temperature range of 773–973 K. Microstructural analysis of the samples before and after annealing was carried out by glancing incidence X-ray analysis (GIXA) and transmission electron microscopy (TEM). GIXA was performed using an 8° incidence angle and CuK $\alpha$  radiation. The chemical composition and crystalline structure were studied using  $\theta$ -2 $\theta$  diffractometer

(Panalytical X-Pert MRD) with a copper X-ray tube working at 40 kV and 30 mA. A parabolic multilayer mirror was used as a secondary optic. Cross-sectional high resolution TEM observations were carried out using a FEI-Tecnai F20-ST at an accelerating voltage of 200 kV. Specimens for the cross-section TEM observations were prepared by the standard procedures of cutting, gluing, mechanical grinding, using a tripod device and Ar-ion sputter thinning.

## Results and Discussions

### Thermal Stability of Si/TaN/Cu and Si/TaN/Ta/TaN/Cu System

The barrier performance of TaN and TaN/Ta/TaN against Cu diffusion is investigated by evaluating the thermal stability of Si/barrier/Cu systems using GIXA, which are carried out for samples before and after being annealed in the 500–700 °C temperature range (Figure 1). The GIXRD pattern of the as-deposited TaN layer reveals that thin  $\delta$ -TaN films with a NaCl type structure are formed (Figure 1a). These TaN films consist of polycrystalline grains with random orientation, as the five major diffraction peaks of the fcc  $\delta$ -TaN phase are observed. The diffraction peaks at  $2\theta$  angles of 43.4, 50.6, and 74.2° are characteristics of the polycrystalline fcc-Cu. Additional diffraction peaks of the cc  $\alpha$ -Ta are observed for the as-deposited TaN/Ta/TaN sample (Figure 1b). These results are in agreement with the preferred growth of  $\alpha$ -Ta deposited onto TaN which is observed by Edelstein et al.<sup>[13]</sup>

No copper silicide peak is observed after annealing at 600 °C for 30 min, for the two diffusion barriers. The increase in the intensity and sharpness of the copper peaks during the annealing indicates the grain growth of the copper layer, which has been previously observed.<sup>[14]</sup> For the Si/TaN/Cu sample, the formation of  $\text{Cu}_3\text{Si}$  precipitates is observed from 700 °C as the diffraction peaks at  $2\theta$  angles of 28.2, 38.3, 44.6, and 45.3° are characteristic of the  $\text{Cu}_3\text{Si}$  phase.<sup>[15]</sup> The formation of copper silicide precipitates is associated with the consumption of copper, which indicates the copper diffusion through the diffusion barrier into silicon substrate. The persistence of copper peaks shows that copper is not completely transformed into silicides after an annealing at 700 °C. As seen in Figure 1b, the X-ray patterns of the TaN/Ta/TaN barrier annealed in the 500–700 °C temperature range are similar to that of the as-deposited one, excepted the increase in

the copper peak intensity with the annealing temperature. Thus, the integrity of the multilayer barrier is still remained stable as no copper silicide forms up to 700 °C for 30 min. It should be noted that for both Si/TaN/Cu and Si/TaN/Ta/TaN/Cu samples, the formation of Ta silicides compounds is not detected, which is similar to that observed in previous investigations.<sup>[5]</sup>

According to GIXA results, the TaN/Ta/TaN multilayer barrier appears to be more efficient in preventing Cu diffusion than the single TaN layer. For the Si/TaN/Cu system, the copper atoms diffuse through the TaN layer to silicon substrate at 700 °C, which results in the failure of the barrier layer by copper silicide formation at the Si/TaN interface. In contrast, a limited diffusion of copper through the TaN/Ta/TaN multilayer is found as no copper silicide precipitates are observed to 700 °C.

### Influence of Annealing on the Microstructure of TaN and TaN/Ta/TaN Barriers

Cross-sectional TEM observations were performed on samples before and after annealing at 700 °C to get more information about the reaction products and the resulting morphology (Figure 2 and 3).

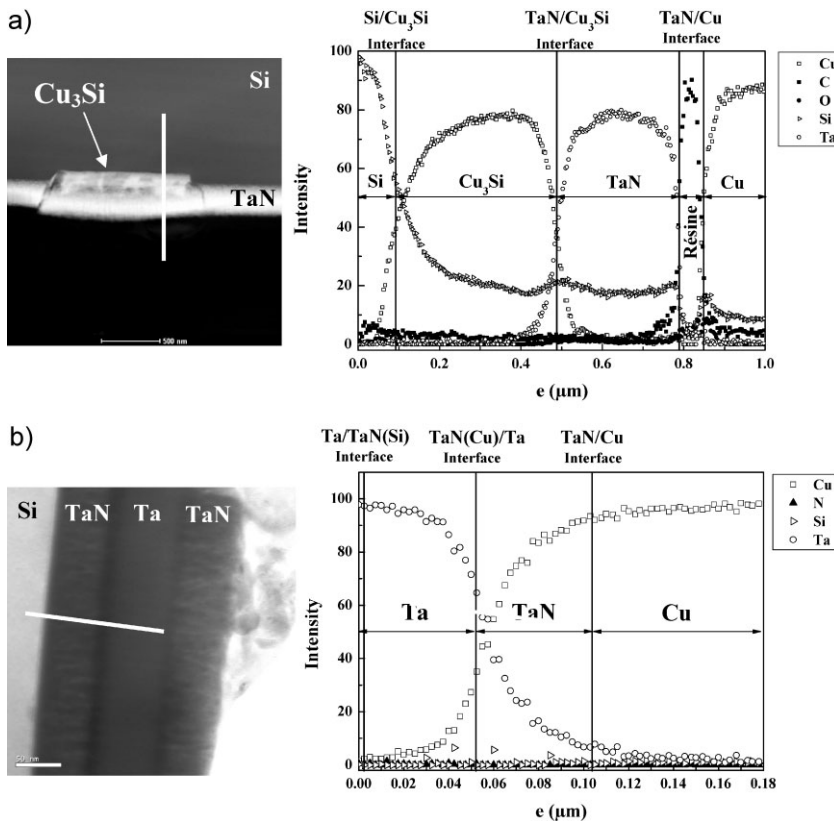


Figure 3. Depth profiles of Cu, Ta, and Si in samples after annealing at 700 °C (a) Si/TaN/Cu (b) Si/TaN/Ta/TaN/Cu.

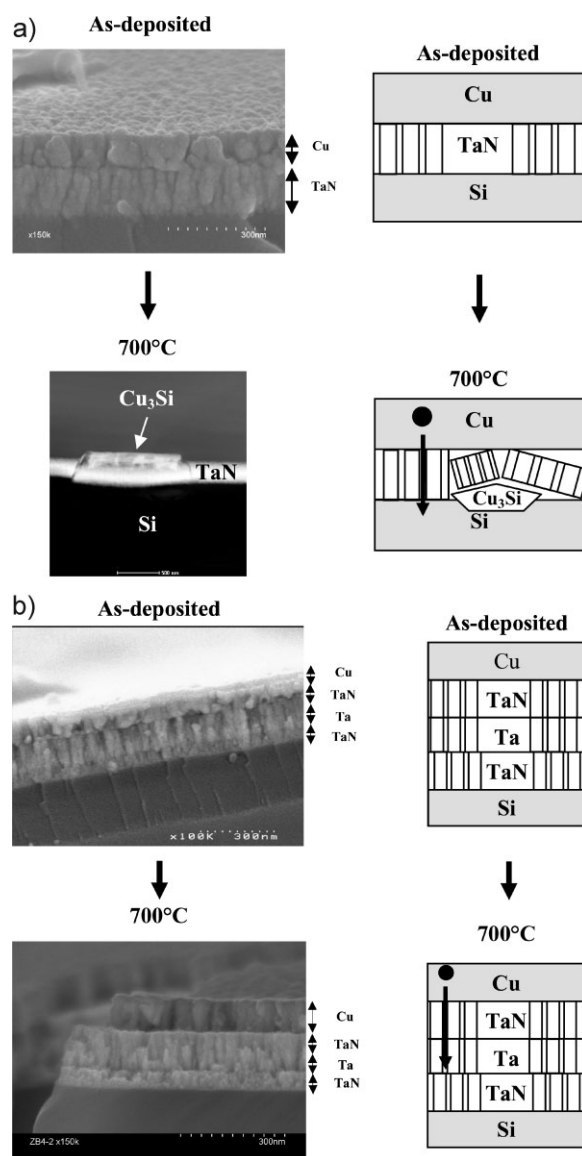
For the as-deposited single TaN layer, TEM observations indicate the columnar growth perpendicular to the substrate surface as evidenced from the coexistence of dark and light contrast areas (Figure 2a). As previously described,<sup>[11,12]</sup> the columnar microstructure is associated with inter-column voids. The high resolution image associated to the Fourier transform pointed out that the as-deposited TaN films are made of crystalline grains, which are embedded in an amorphous phase (not shown here). The crystalline structure was identified to the NaCl structure of the  $\delta$ -TaN phase. The interplanar spacings are therefore calculated to be 0.25, 0.22, and 0.15 from the Fourier transform. For the as-deposited Si/TaN/Ta/TaN/Cu sample (Figure 2b), the interfaces between the different films are flat and clear, the Ta and TaN layers can be distinguished by the different contrast. It can be observed that each layer in the multilayer barrier exhibits a columnar growth. It is also shown that the TaN/Ta/TaN barrier consists of the fcc  $\delta$ -TaN phase as well as cc  $\alpha$ -Ta.

Transmission electron microscopy (TEM) observations of the Si/TaN/Cu sample after annealing at 700 °C for 30 min are shown in Figure 3a. Precipitates are observed at the Si/TaN interface, indicating severe reaction of Si/TaN/Cu. To determine the composition of precipitates, EDS depth profiles were performed from the TaN/Cu interface to silicon substrate (Figure 3a). The depth profiles of Cu, Ta, and Si reveal that the precipitates consist of copper and silicon elements and are a copper rich region. The formation of these precipitates may be attributed to copper diffusion through TaN barrier layer and reaction with silicon substrate to form  $\text{Cu}_3\text{Si}$  compounds, which is consistent with the GIXA results. The nucleation of  $\text{Cu}_3\text{Si}$  precipitates is associated with a large volumic expansion of 150%, leading to multicracks of the barrier layer.<sup>[3]</sup> Figure 3b shows the TEM observations and analysis of the multilayer sample annealed at 700 °C. The TaN/Si interface of the annealed sample remains as flat as the as-deposited sample, the Ta and TaN layers can be still distinguished and the columnar growth is conserved. No copper silicide precipitates are observed. According to the EDS depth profile (Figure 3b), the diffusion distance is found to be 100 nm after annealing at 700 °C during 30 min. Indeed, the copper atoms penetrate the multilayer barrier at the interface Cu/TaN, diffuse through the TaN(Cu) and Ta layers and stop at the Ta/TaN(Si) interface. Also, a significant amount of Cu remains at the sample surface. Therefore, the multilayer barrier may be supposed to reduce the copper diffusion to silicon substrate after annealing at 700 °C. This may be explained by the difference in microstructure of the two diffusion barriers, which will be discussed in the next section.

### Diffusion Mechanism

According to microstructural analysis, the TaN/Ta/TaN multilayer appears to have much better barrier perfor-

mance than the single TaN layer. It may be supposed that microstructure is important to the stability of TaN and TaN/Ta/TaN thin films as diffusion barriers. The thermal stability of these barriers will be discussed by referring to schematically cross-section of the sample structures, which are deduced from the microstructural analysis (Figure 4). Each single TaN or Ta layer is deposited with a characteristic columnar structure, in which inter-column voids are parallel to each other and perpendicular to the substrate. These inter-column voids may be assumed to create fast diffusion paths through which copper atoms migrate to the silicon substrate.<sup>[12]</sup> That is the reason why TaN/Ta/TaN multilayer barrier are sputter deposited to obtain non-straight diffusion paths.



**Figure 4.** Schematic illustrations of the cross-sectional microstructure of samples in the as-deposited state and after annealing at 700 °C – 30 min<sup>-1</sup> (a) Si/TaN/Cu (b) Si/TaN/Ta/TaN/Cu.

The chemical inertness of the two diffusion barriers with Si and Cu at elevated temperatures is confirmed. Indeed, at the Cu/barrier and barrier/Si interfaces, no reaction between the Cu or Si and the barrier are observed after annealing at 700 °C for 30 min. These results are in agreement with the work of Yan and Chang<sup>[16]</sup> and Hubner et al.<sup>[15]</sup> It has been reported that TaN does not form intermetallic compounds with copper and the Ta/Si reactivity decreases in the presence of N.

The best thermal stability is obtained in the TaN/Ta/TaN multilayer barrier. Indeed, for the single TaN layer, the copper atoms penetrate the diffusion barrier via the inter-column voids at the Cu/TaN interface from 600 °C. At 700 °C, the linearly motion of copper through the columnar structure results in formation of Cu<sub>3</sub>Si precipitates at the TaN/Si interface, leading to the failure of the barrier layer. Thus, the reacted structure consists of Si–Cu<sub>3</sub>Si–TaN (Figure 4a). In contrast, a change in the Cu diffusion mechanism is observed for the multilayer barrier. A limited copper diffusion through TaN/Ta/TaN barrier occurs since no copper silicide precipitates are observed up to 700 °C for 30 min and a significant amount of copper remains at the sample surface. It has been shown that copper diffuses through the barrier layer and stops at the Ta/TaN(Si) interface at 700 °C. This may be explained considering the non-continuous columnar growth of the multilayer barrier, which results in non-linear diffusion paths (Figure 4b).

## Conclusion

The diffusion of copper to silicon substrates through single TaN layer and novel TaN/Ta/TaN multilayer is studied. The thermal stability and barrier effectiveness of the two metallization schemes have been compared by evaluating the interfacial reactions and the resulting morphology after 30 min of annealing at temperatures from 500 to 700 °C. A thermally stable Si/Cu contact system with TaN/Ta/TaN multilayer barrier is successfully demonstrated. Regarding the single TaN barrier, it appears that the TaN barrier prevents the Cu diffusion into the Si substrate after annealing at 600 °C for 30 min. The mechanism by which the TaN barrier fails involves the motion of Cu through columnar structure, via the inter-column voids to form Cu<sub>3</sub>Si precipitates. Thus, the columnar microstructure of the layers is supposed to be important to the stability of the TaN thin films as a diffusion barrier. A change in the Cu diffusion mechanism is observed for the multilayer. The TaN/Ta/TaN layer for use as a diffusion barrier may allow to create inter-

column voids mismatch at the interfaces between the different layers, which results in non-linear diffusion paths. Further investigations will be necessary for a better understanding of the role of the multilayer barrier on the diffusion mechanisms. These results constitute the basic information that will be benefit for future diffusion simulation.

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