

# Different SiH<sub>4</sub> treatments of CVD TiN barrier layers for Cu Metallization

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## 1 Introduction

The ITRS 2003 predicts for interconnects a reduced diffusion barrier thickness of a few nanometers in the next years. But the film thickness reduction involves an increased defect density. Particularly with regard to crystalline barriers like TiN the diffusion path along the grain boundaries is drastically shortened.

The TiN barrier performance can be enhanced by silane treatments. On the one hand the silane treatment could lead to Si-N formation, so that the TiN grains are embedded in amorphous SiN. On the other hand the Si introduction in the barrier results in higher electrical resistivity.

## 2 Experimental

The experiments were carried out in a lamp-heated tungsten CVD chamber of an applied Materials 5000™ cluster tool. The TiN layers were produced by a multistep process consisting of alternating MOCVD deposition steps and H<sub>2</sub>/N<sub>2</sub> plasma treatment steps. The pyrolysis of tetrakis(dimethylamino)titanium (TDMAT) at substrate temperatures of 350°C is used for the deposition step. The density, microstructure, composition and consequently the electrical resistivity and barrier performance are strongly affected by the plasma treatment parameters [2]. This TiN contains grains reaching nearly from the bottom to the top of the entire film thickness which means there is no interruption of grain growth by the multiple deposition process.

Marcadal et al. [3] investigated silane soaks after each full cycle and for not plasma treated TiN films to exemplify the insufficient densification at the sidewalls of vias and trenches. In the case of plasma treated Ti(Si)N films the grains are smaller than for pure TiN and are confined to a single cycle layer. But the Si amount is smaller (4 %) than in the not plasma treated TiN (7 %).

We investigated silane treatments integrated as soak but also as plasma at different times in the TiN deposition cycle:

TiSiN 1	10 s SiH <sub>4</sub> plasma between pyrolysis and H <sub>2</sub> /N <sub>2</sub> plasma
TiSiN 2	10 s SiH <sub>4</sub> soak between pyrolysis and H <sub>2</sub> /N <sub>2</sub> plasma
TiSiN 3	30 s SiH <sub>4</sub> plasma instead of H <sub>2</sub> /N <sub>2</sub> plasma
TiSiN 4	10 s plasma after a full cycle

The integration in the whole process was done for a 3 cycle process to obtain thin films ≤ 10 nm and only the middle cycle was treated with SiH<sub>4</sub>.

## 3 Results

For all SiH<sub>4</sub> treatments the deposited film thickness and the electrical resistivity were partly drastically increased compared to untreated TiN. Only TiSiN 2 with the SiH<sub>4</sub> soak results in moderate thickness and electrical resistivity.

Table 1: Electrical resistivity of the SiH<sub>4</sub> treated TiN compared to TiN in the same thickness range

TiSiN process	$\rho_{\text{TiSiN}}$ [ $\mu\Omega\text{cm}$ ]	$\rho_{\text{TiN}}$ [ $\mu\Omega\text{cm}$ ]	d [nm]
TiSiN 1	689	175	16,8
TiSiN 2	334	260	8,5
TiSiN 3	1605	130	26,2
TiSiN 4	542	225	14

In case of the SiH<sub>4</sub> plasma treatments the clearly higher thickness is caused by the deposition of a Si interlayer. The thickness of these Si layers depends on the SiH<sub>4</sub> plasma treatment time. The replacement of the H<sub>2</sub>/N<sub>2</sub> plasma by SiH<sub>4</sub> plasma leads to 13 nm Si deposition and thus to highest thickness of the whole layer. The SiH<sub>4</sub> plasma onto the not densified TiN layer (TiSiN 1 and TiSiN 3) yielded nearly no densification of these cycle layers. These layers remain amorphous in comparison with the first cycle layer. Also the middle cycle layer of TiSiN 2, SiH<sub>4</sub> soak onto the not densified layer with followed H<sub>2</sub>/N<sub>2</sub> plasma, is thicker and appears more amorphous than the other cycle layers. Because of the H<sub>2</sub>/N<sub>2</sub> plasma after the SiH<sub>4</sub> soak the formation of SiN bonds is more likely as the TOF-SIMS results confirm.

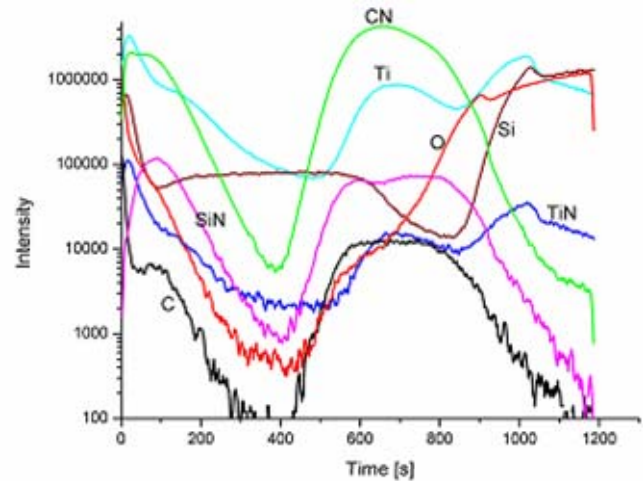
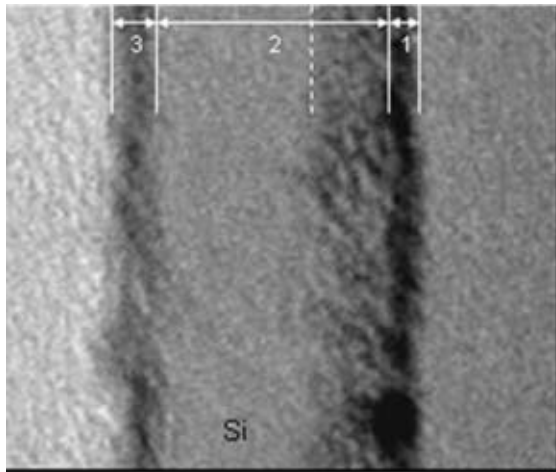


Fig. 1: TiSiN 3 ( $\text{SiH}_4$  plasma instead of  $\text{H}_2/\text{N}_2$  plasma) TEM image and TOF-SIMS graph

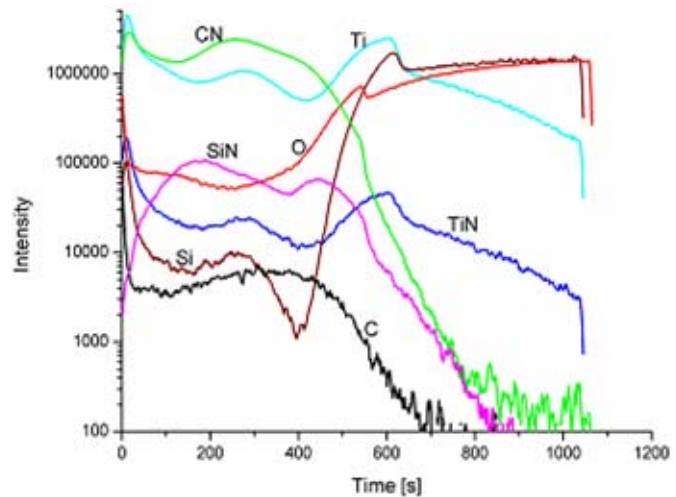
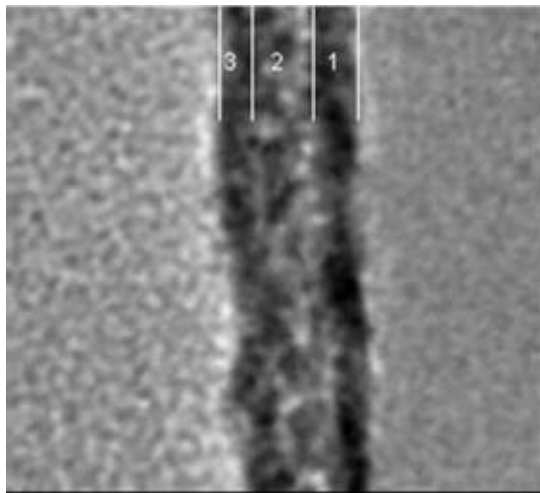


Fig. 2: TiSiN 2 ( $\text{SiH}_4$  soak between pyrolysis and  $\text{H}_2/\text{N}_2$  plasma) TEM image and TOF-SIMS graph

By the same evidence the layers from the 3<sup>rd</sup> cycle in all  $\text{SiH}_4$  treatment variants seem less crystalline than the layers from the first cycle. Probably, here the Si from the foregoing cycle is incorporated during the pyrolysis of TDMAT in the layer and inhibits a continuous crystallisation.

Apart from the Si deposition of the  $\text{SiH}_4$  plasma treatments, these treatment variants are not qualified for the improvement of barrier performance. The efficiency of the plasma at the sidewall is reduced because of the direction dependent impact of plasma.

A thermal silane treatment is more suitable to stabilize the TiN barrier. The electrical resistivity

is only slightly increased and the grain growth is inhibited by the SiN formation.

Further investigations will be performed to examine the thermal stability and barrier efficiency of the developed Ti(Si)N films.

## References:

- [1] ITRS 2003 update, Int. Sematech & SIA, Austin, Texas (2003); [www.public.itrs.net](http://www.public.itrs.net)
- [2] Riedel, S.; Schulz, S.E.; Gessner, T.; *Microelectr. Eng.* 50 (2000) 533-540
- [3] Marcadal, C.; Eizenberg, M.; Yoon, A.; Chen, L.; *J. Electrochem. Soc.* 149 (1) (2002) C52-C58