

Electroless Plating of Copper on Metal-Nitride Barrier Films

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Electroplating of Cu is one of key technology in multilevel interconnections in ultra large scale integrated (ULSI) circuits. However, sputtered Cu seed layer deposition prior to electroplating faces to an inherent difficulty in continuity at the sidewalls of high aspect ratio holes. Electroless Cu deposition on metal nitride diffusion barriers is attractive because of its high performance of conformal deposition.^{1,2} In recent years, a wet activation process called displacement deposition has been reconsidered and developed to activate diffusion barriers in acidic solution.³ In this paper, we report a method of direct electroless copper plating on a barrier layers of TaN, TiN or WN and discuss the deposition mechanisms.⁴

TiN/Ti/SiO₂/Si, TaN/SiO₂/Si and WN/SiO₂/Si substrates were used for the electroless copper plating. The plating solution was composed of glyoxylic acid as a reducing agent and TMAH as a pH control. When the TiN, TaN and WN substrates were properly pretreated to remove the surface oxygen-rich layer and were immersed into an electroless Cu plating solution with glyoxylic acid, the electroless-plated copper was able to be deposited on the barrier layers without any Pd catalysis adsorption treatment. The deposition rates of electroless copper plating for the various barrier layers were measured by cross-sectional scanning electron microscopy (SEM) observations and the copper film thickness vs. plating time is shown in Figure 1. Cu was deposited on TaN and WN from the beginning of immersion, while in the case of TiN, the Cu deposition started after 5 minutes had passed.

In order to understand the deposition mechanisms of electroless copper plating, the static REDOX (reduction oxidation) potentials of the TaN, TiN and WN films and Cu plate in the plating solution were measured as shown in Table 1. Although the mechanism of electroless copper plating is complex and involves various factors, the static REDOX potentials of all the metal nitride barrier layers that were pretreated were lower than that of the copper, which meant that displacement plating between Cu²⁺ and metal nitride was thermodynamically feasible. When the barrier layers were immersed into an electroless plating solution that excluded only the reducing agent of glyoxylic acid, the metallic copper was detected by XPS on the surfaces of TaN and WN, although it was not detected on the surface of TiN even after a long plating time (see Table 2). Takano reported that when Si was oxidized to form SiO₂ in plating solution and released free electrons, they reduced Cu²⁺ to metallic copper.⁵ To check the effect of backside Si oxidation to Cu²⁺ reduction, we protected the surface of backside SiO₂ by coating a wax. When the wax-coated substrates were immersed into an electroless plating solution, electroless plated copper did not deposited on the surface of TiN, while it deposited on TaN and WN. Therefore, we may conclude that the deposition mechanism of electroless copper plating on TaN and WN are displacement reactions between TaN or WN with Cu²⁺. For TiN substrate, the deposition mechanism of copper plating is related to oxidation of Si at backside.

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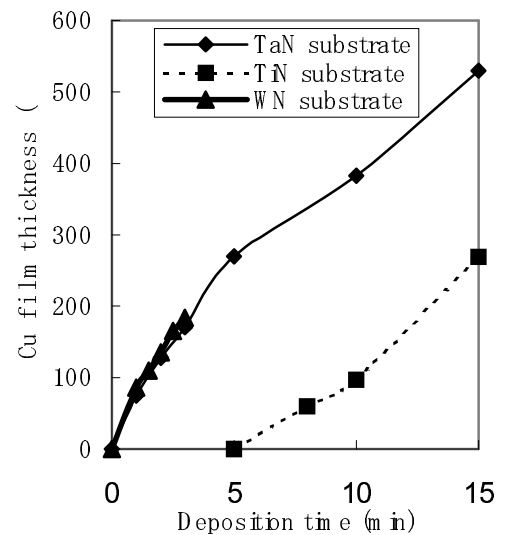


Figure 1. The dependence of electroless copper film thickness vs. plating time. Plating condition: bath temperature 70 °C and pH 12.5 for TaN and TiN substrates, 60 °C at pH 12.5 for WN. substrate.

Table1. The REDOX potential of TiN, TaN and WN Metal-nitrides in plating solution at 40°C|

Electrode	REDOX Potential (mV)
Cu (HCl etching)	167
TiN (before etch)	72
TiN (etched)	117
TaN (before etch)	202
TaN (etched)	-184
WN (after ultrasonic rinse)	-157

Table 2. The change of atomic ratio of Cu to barrier metal with plating time for TiN, TaN and WN substrates

Plating time(min)	Cu/Ta	Cu/Ti	Cu/W
0	0	0	0
1	1.05	0.10	7.62
2	2.02		15
4	3.70	0.13	33.9
8		0.08	
15		0.13	
25		0.14	