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# Effects of Hydrogen Plasma Treatment of the Underlying TaSiN Film Surface on the Copper Nucleation in Copper MOCVD

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**ABSTRACT**

MOCVD is one of the major deposition techniques for Cu thin films and Ta-Si-N is one of promising barrier metal candidates for Cu with high thermal stability. Effects of hydrogen plasma pretreatment of the underlying Ta-Si-N film surface on the Cu nucleation in Cu MOCVD were investigated using scanning electron microscopy, X-ray photoelectron spectroscopy and Auger electron emission spectrometry analyses. Cu nucleation in MOCVD is enhanced as the rf-power and the plasma exposure time are increased in the hydrogen plasma pretreatment. The optimal plasma treatment process condition is the rf-power of 40 W and the plasma exposure time of 2 min. The hydrogen gas flow rate in the hydrogen plasma pretreatment process does not affect Cu nucleation much. The mechanism through which Cu nucleation is enhanced by the hydrogen plasma pretreatment of the Ta-Si-N film surface is that the nitrogen and oxygen atoms at the Ta-Si-N film surface are effectively removed by the plasma treatment. Consequently the chemical composition was changed from Ta-Si-N(O) into Ta-Si at the Ta-Si-N film surface, which is favorable for Cu nucleation.

***Key words* : *Cu MOCVD, Ta-Si-N barrier metal, Plasma treatment, Cu nucleation***

## 1. Introduction

Cu is now widely used as an interconnection material in integrated circuits.[1] Metal Organic Chemical Vapor Deposition (MOCVD) is also considered as an important deposition technique for copper films although electroplating is recently more widely employed in semiconductor industry. A diffusion barrier is necessary between Cu and $SiO_2$ since Cu is very mobile in metals, oxides and semiconductors even at quite modest temperatures, which causes degration of device reliability.[2] Although the chemical stability of polycrystalline TiN which has been used in Al metallization is superior, it has been reported that Cu diffuses through the grain boundary of TiN to the Si substrate and results in barrier failure.[3] On the other hand, amorphous thin films are an attractive alternative to polycrystalline thin films because of the absence of grain boundary for diffusion, since most barrier failures occur along grain boundaries. Recently, ternary amorphous thin films such as M (M = Ta, W, Mo, Ti)-Si-N have been studied as extremely promising candidates for diffusion barrier due to its higher thermal stability against Cu diffusion.[4-12] Among these, the one with the highest thermal stability has been reported to be Ta-Si-N.[4] In this communication we report on the effect of plasma treatment of the underlying TaSiN film sample on the Cu nucleation in Cu MOCVD. Unless the underlying barrier metal is treated with plasma prior to the Cu deposition by MOCVD, Cu nucleation will be very low, so that a continuous Cu film will be difficult to form.[13] Therefore, pretreatment of the TaSiN film surface is essential in Cu MOCVD to enhance Cu nucleation. We reported Pd sputtering pretreatment previously and we report hydrogen plasma pretreatment in this paper.

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## 2. Experimental Procedure

Substrates of 5 Ωcm n-type (100) Si were cleaned in a dilute HF solution (HF : $H_2O$=1 : 20) for 2 min and rinsed in deionized water and subjected to $N_2$ blowing before being loaded into the deposition chamber. Ta-Si-N films with the thickness of approximately 100 nm were deposited on the Si substrates by reactive DC magnetron sputtering using $Ta_3Si_3$ target in Ar and $N_2$ gas mixture. Then the Ta-Si-N film surfaces were treated with hydrogen plasma. The standard process parameters for the plasma cleaning were the rf-power of 40 W, the plasma exposure time of 5 min, the $H_2$ flow rate of 100 sccm and the cleaning temperature of 298 K. The rf-power and the exposure time were varied in the ranges of 20 – 200 W and 1 – 15 min, respectively.

After plasma treatment, Cu films were deposited on the TaSiN films by MOCVD. The process parameters for the Cu MOCVD were the substrate temperature of 180°C, the base vacuum of $10^{-5}$ torr, and the deposition time of 20 min. Cu(I)(hfac) vinyl-tyi-methyl-silane was introduced with 50 sccm Ar as a carrier gas through a mass flow controller,

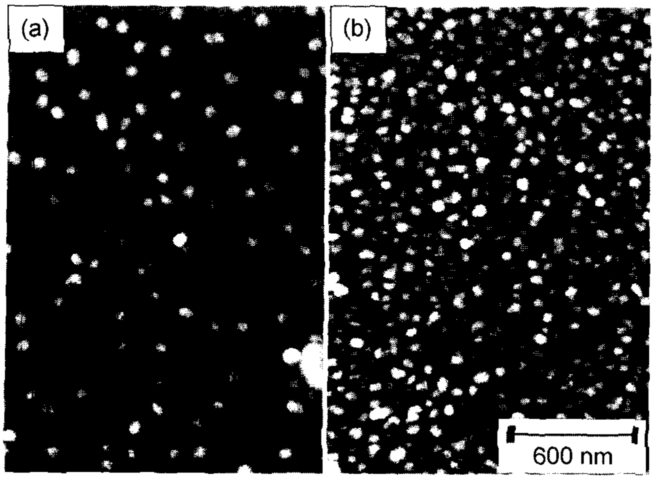


**Fig. 1.** SEM micrographs of Cu particles deposited by MOCVD on the Ta-Si-N film for different plasma exposure times : (a) 30 s and (b) 8 min in the hydrogen plasma pretreatment.

and this reactant gas was introduced vertically from the gas shower head toward the wafer surface. The precursor bubbler and line temperatures were held at 50 and 60°C to prevent condensation, respectively.

Effects of plasma pretreatments to the TaSiN film surface on Cu nucleation were investigated. Scanning Electron Microscopy (SEM) was used to measure the Cu nucleation density and to observe the morphology of the Cu film. X-ray Photoelectron emission Spectroscopy (XPS) and Auger depth profiling analyses were used to investigate the bonding state of atoms and the concentrations of oxygen and nitrogen at the TaSiN film surface, respectively.

## 3. Results and Discussion

By comparing the SEM micrographs in Fig. 1(a) and (b) of the Cu particles deposited by MOCVD for 20 min on the Ta-Si-N substrate with different times of the hydrogen plasma pretreatment, we can see that Cu nucleation is substantially enhanced by treating the Ta-Si-N film surface with hydrogen plasma prior to Cu MOCVD. Fig. 2(a) and (b) show dependences of Cu nucleation density on the plasma exposure time and the rf-power for Cu MOCVD conducted on the Ta-Si-N film after pretreatment of the Ta-Si-N film surface with hydrogen plasma. The Cu nucleation density represents the number of Cu particles per unit area in SEM micrographs. The Cu nucleation density tends to increase with the increase of the rf-power in the plasma pretreatment and be saturated at the rf-power of 40 W (Fig. 2(a)). On the other hand, the Cu nucleation density tends to increase as the plasma exposure time increases and be saturated at the exposure time of 2 min (Fig. 2(b)). The Ta-Si-N film surface seems to be saturated with Cu particles after Cu MOCVD for 20 min on Ta-Si-N film treated with hydrogen plasma for 2 min at 40 W. However, it is not desirable to increase the exposure time above 2 min and the rf-power

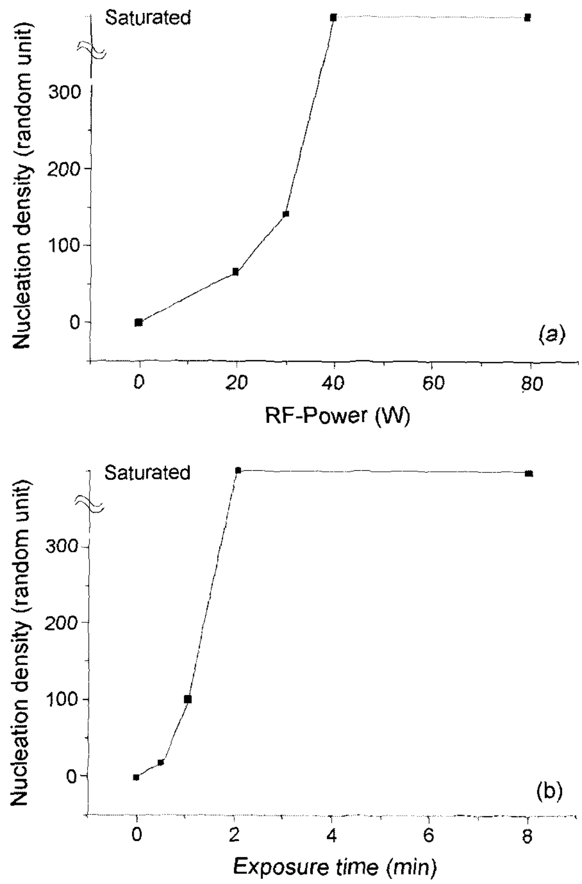


**Fig. 2.** The nucleation density of Cu vs (a) the rf-power and (b) the exposure time of the hydrogen plasma treatment.

above 40 W since higher rf-power and longer plasma exposure time not only would make the Ta-Si-N film surface rougher and maybe aggravate the plasma radiation damage on the Si substrate but also would not enhance Cu nucleation very much. The dependence of the Cu nucleation in Cu MOCVD on the hydrogen gas flow rate in the hydrogen plasma treatment was found to be low. To control the process parameters for Cu MOCVD would be much more efficient in increasing the Cu film thickness than to increase the rf-power or plasma exposure time for the plasma pretreatment further.

The XPS spectra in Fig. 3(a)-(c) and AES depth profiles in Fig. 4(a),(b) may help us understand the mechanism through which Cu nucleation is enhanced by pretreating the underlying Ta-Si-N film surface with hydrogen plasma. Both the $Ta_{4f}$ intensity peak (Fig. 3(a)) and $Si_{2p}$ intensity peak (Fig. 3(b)) nearly do not change, but the $N_{1s}$ intensity peak distinctly decreases (Fig. 3(c)) with increasing the rf-power or the plasma exposure time in plasma pretreatment. AES analysis results (Fig. 4(a)) show the same trends as the XPS analysis results. Nitrogen concentration at the surface of the Ta-Si-N film markedly decreases as the plasma exposure time in the hydrogen plasma treatment increases. Also the AES depth profiles in Fig. 4(b) show that oxygen concentration at the surface of Ta-Si-N film decreases as the

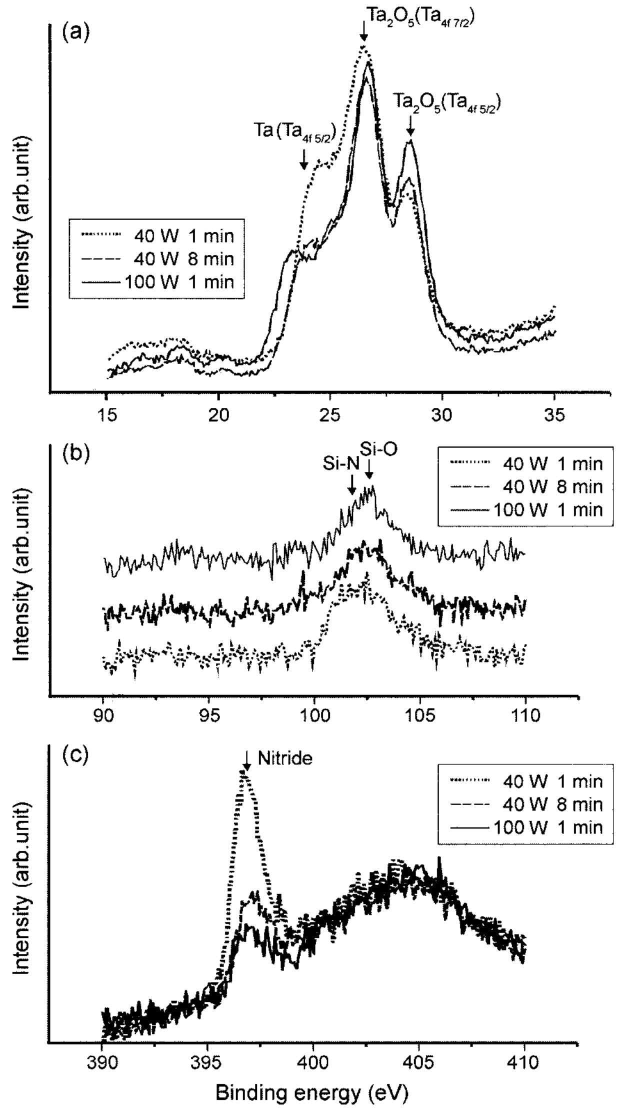


**Fig. 3.** XPS spectra of the Cu/Ta-Si-N/Si(100) sample for different plasma exposure times and rf-powers in hydrogen plasma pretreatment : (a) Ta 4f peak, (b) Si 2p peak, and (c) N 1s peak.

plasma exposure time increases, suggesting that hydrogen plasma treatment removes the oxygen atoms adsorbed by the Ta-Si-N film surface. From these analysis results one may extract two conclusions that Ta-Si-N changes to Ta-Si by hydrogen plasma treatment and that oxygen atoms adsorbed at the Ta-Si-N film surface are also removed by hydrogen plasma treatment.

## 4. Conclusions

Cu nucleation in Cu MOCVD is effectively enhanced by treating the underlying Ta-Si-N film surface with hydrogen plasma prior to Cu MOCVD. The Cu nucleation density in Cu MOCVD increases as the rf-power and the plasma exposure time increase in the hydrogen plasma pretreatment, but it is saturated at the rf-power of 40 W and the plasma

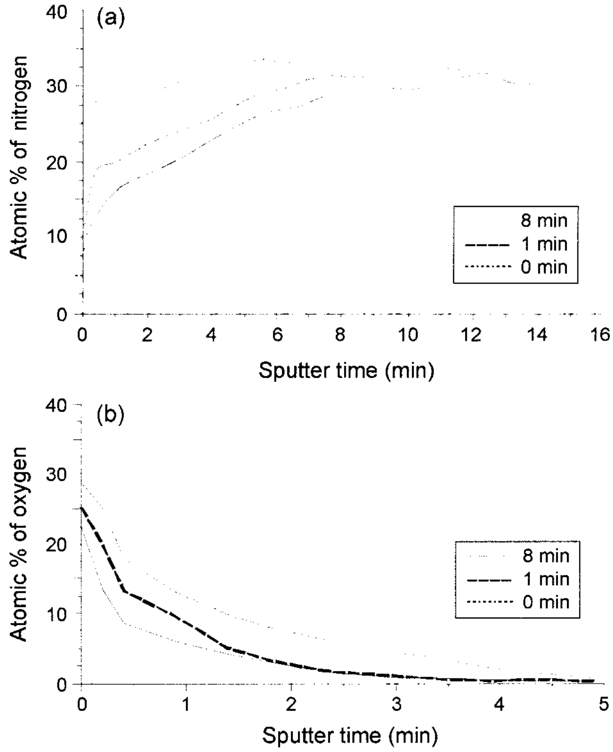


**Fig. 4.** AES depth profiles of (a) nitrogen and (b) oxygen for the Ta-Si-N film surface after hydrogen plasma treatment with different plasma exposure times at a fixed rf-power of 40 W.

exposure time of 2 min. To increase the rf-power and the plasma exposure time further would increase the plasma radiation damage for the Si substrate. Therefore, 40 W and 2min are the optimal process conditions for the hydrogen pretreatment. The mechanism through which Cu nucleation is enhanced by hydrogen plasma pretreatment is that the plasma treatment removes the nitrogen and oxygen atoms from the Ta-Si-N film surface. Since Ta-Si is a substrate more favorable for Cu nucleation than Ta-Si-N(O), Cu nucleation on the Ta-Si-N film is enhanced by hydrogen plasma pretreatment of the Ta-Si-N film surface.

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