The CVD Growth of Cu Films using H_2 as Carrier Gas

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Copper chemical vapor deposition from Cu(hexafluoroacetylacetonate)trimethylvinylsilane (Cu(hfac)TMVS) was studied using a low pressure chemical vapor deposition system of a cold wall vertical reactor. The Cu films deposited using H_2 as a carrier gas revealed no impurities in the films within the detection limits of Auger electron spectroscopy and x-ray photoelectron spectroscopy. Using hydrogen as a carrier gas, the hydrogen not only acts as a reducing agent, but also reacts with the residual fragment of precursor. As a result, using H_2 as a carrier gas for Cu(hfac)TMVS resulted in Cu films of lower resistivity, denser microstructure and faster deposition rate than using Ar or N_2 as the carrier gas. Moreover, we found that N_2 plasma treatment on the substrate surface prior to Cu deposition increased the deposition rate of Cu films.

Key words: Chemical vapor deposition (CVD), Cu films, H_2 as carrier gas, resistivity

INTRODUCTION

With the continuing progress of ultra large scale integrated (ULSI) circuits, the feature sizes of vias and holes in multilevel metallization structures have decreased to sub-quarter micron, while the associated aspect ratios have increased to four and higher. Eventually, however, the continuing scale down of active devices becomes less profitable, as the limitations of the circuit speed and maximum functional density become more dependent on the characteristics of interconnects than on the scaled devices. Thus, the conventional physically vapor deposited, aluminum-based interconnect scheme faces various performance and reliability challenges.[1–4] Hence, new interconnect metals and their processing techniques must be studied and developed. Chemical vapor deposition of copper has been one of the most promising approaches. Copper has a resistivity lower than aluminum (bulk resistivity of 1.7 vs 2.7μ Ω-cm), which significantly reduces the RC time delay. The electro/stress migration resistance of copper has been reported to be two orders of magnitude better than that of aluminum, and thus higher reliability and improved performance can be expected by using copper interconnects.[5–7] Moreover, it has been demonstrated that the technique of chemical vapor deposition (CVD) of copper possesses an intrinsic potential for void free filling of aggressive via and hole structures at near bulk resistivity and high growth rates.[8,9]

However, in spite of significant progress in the development of copper based metallization schemes, several key processing and reliability issues remain to be resolved before copper technology becomes an industrial reality. Among them, the development of a CVD process capable of depositing high purity and dense films of copper with controlled microstructure at relatively low temperatures with high deposition rates is of vital interest for practical applications.

In this work, copper chemical vapor deposition from Cu(hexafluoroacetylacetonate) trimethylvinylsilane (Cu(hfac)TMVS)[10,11] was studied with emphasis on the role of H_2 as a carrier gas. The effects of substrate surface treatment by N_2 plasma were also investigated.

EXPERIMENT

A cold-wall, low pressure CVD system of vertical reactor was employed to deposit Cu films using Cu(hfac)TMVS as the precursor. The Cu films were deposited on TiW substrates. A TiW layer of 100 nm thickness was deposited on p-type, (100)-oriented Si wafers by sputtering using a TiW (Ti 10 wt%) target in an Ar ambient at a pressure of 5×10^{-3} Torr and with a deposition rate of 10 nm/min. The base pressure prior to the sputter deposition was 1.2×10^{-6} Torr. The TiW substrates were cleaned in acetone for 10 min

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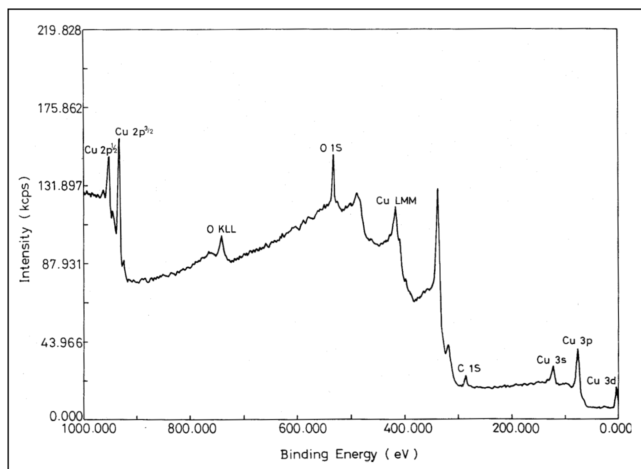


Fig. 1. XPS spectrum of as-deposited Cu films on TiW substrates.

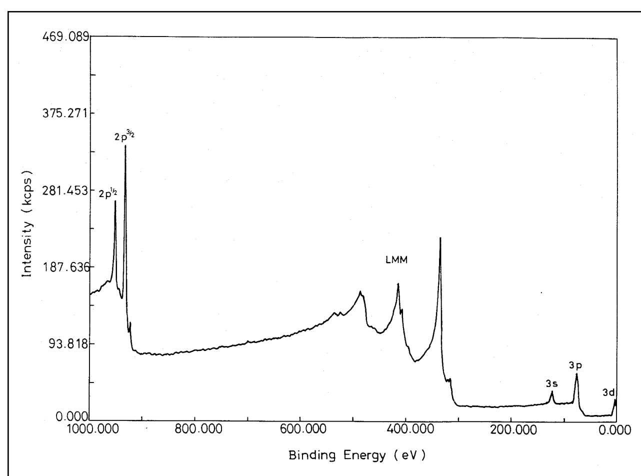


Fig. 2. XPS spectrum of Cu films on TiW substrates after removal of about 25 nm thick surface layer by Ar-ion sputtering.

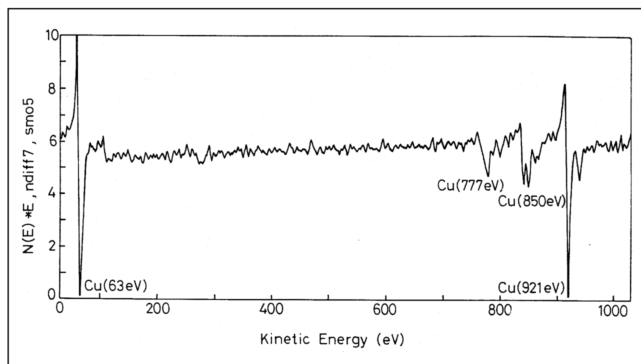


Fig. 3. Typical differential AES spectrum of Cu films on TiW substrates after removal of about 25 nm thick surface layer by Ar-ion sputtering.

and then rinsed in deionized water for 5 min. The substrates were then dried with N_2 gas and immediately loaded into a loading chamber before they were loaded in the CVD chamber. When the loading chamber was pumped down to a pressure of 10^{-7} Torr, which is nearly equal to the pressure in the reaction chamber, the substrates were transferred to the substrate holder in the reaction chamber. The Cu

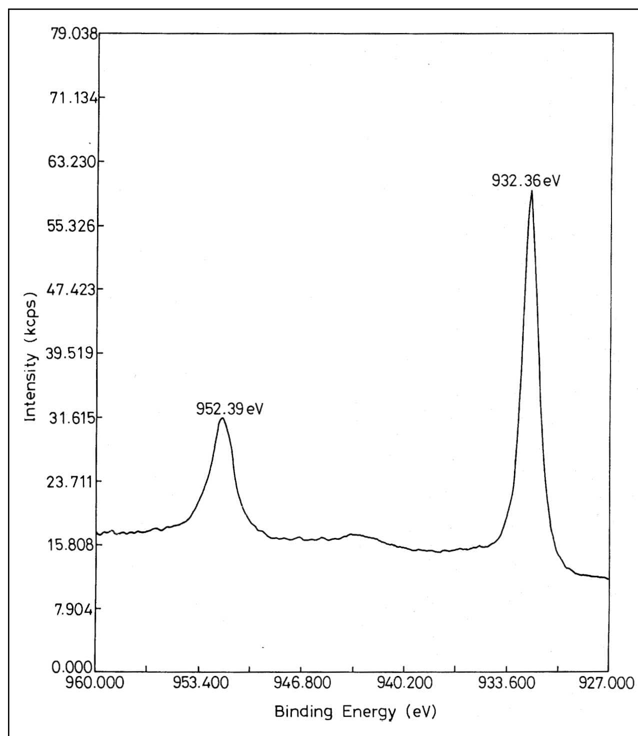


Fig. 4. XPS spectrum of Cu films showing Cu($2p_{1/2}$) and Cu($2p_{3/2}$) peaks.

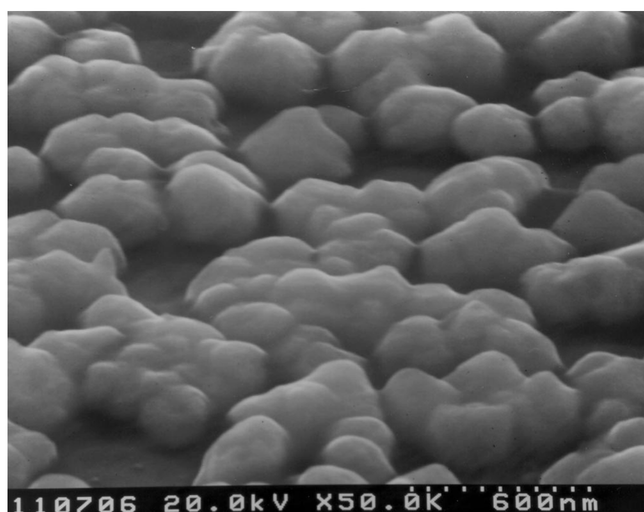
CVD was performed over a temperature range of 160 to 240°C and a pressure range of 70 to 1000 mTorr. In this study, the precursor was maintained at a temperature of 40°C, and the carrier gas (H_2, Ar or N_2) was bubbled through the liquid Cu(hfac)TMVS precursor to carry the Cu source into the reaction chamber via a delivery line kept at a temperature of 60°C. When the deposition was completed, the samples were cooled in the ambient of carrier gas at a pressure of 10 Torr.

The Cu film thickness was measured using a Dek-Tek profiler on a step created on the film and was further confirmed by the cross-sectional scanning electron microscope (SEM) examination. A four-point probe was employed to measure the sheet resistance. SEM was also used to observe the surface morphology of the Cu films. Both Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to analyze the impurity content in the Cu films. Transmission electron microscope (TEM) was used to examine the microstructure of the Cu films, and x-ray diffiaction (XRD) analysis was used for crystal phase identification.

RESULTS AND DISCUSSION

Copper films were deposited to thicknesses of 0.5 to 1.0 μm on TiW substrates with good adhesion; the thickness of the films deposited were measured using a Dek-Tek profiler on a step created on the film and were confirmed by SEM examination. The as-deposited Cu films revealed carbon (C) and oxygen (O) contamination on the surface regions, as shown in the XPS spectrum of as-deposited Cu films illustrated in

Fig. 1. After argon-ion sputtering to remove the surface layers of about 25 nm thickness, all evidence of C and O contamination disappeared within the detection limits of XPS and AES, as shown in the XPS and AES spectra in Fig. 2 and Fig. 3, respectively. The high resolution $Cu(2p_{1/2})$ and $Cu(2p_{3/2})$ peaks with binding energies of 952.39 and 932.36 eV, respectively, as shown in Fig. 4, are consistent with the reported values.[12] This indicates that the impurities incorporated into the bulk of Cu films during the film deposition were minimal. The contamination of C and O on the surface layers of as-deposited Cu films were presumably due to the adsorption of residual gases during the cooling stage of Cu films. This is surmised because, samples were retained in the deposition chamber and cooled in the ambient of carrier gas at a pressure of 10 Torr post Cu deposition.



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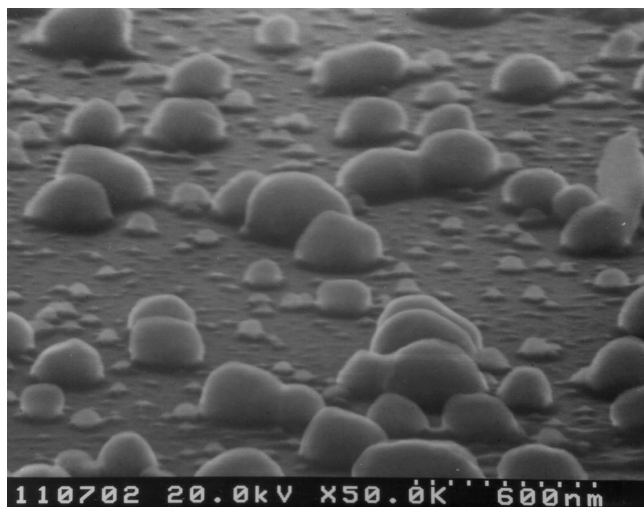


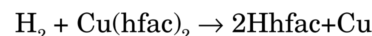
b

Fig. 5. SEM micrographs of Cu films deposited on TiW at 200°C and 500 mTorr using (a)H_2 and (b)Ar as the carrier gas; the flow rate of carrier gas is 20 sccm and the deposition time is 10 min.

Table I. Deposition Rate and Electrical Resistivity of Cu Films Deposited using Different Carrier Gases

Carrier Gas	H_2	Ar	N_2
Resistivity (μΩ-cm)	2.85	4.5	3.3
Deposition Rate (Å/min)	162	128	145

Copper films were also deposited using Ar as well as N_2 as a carrier gas. We found that the Cu films deposited using different carrier gases and the Cu films deposited on different substrates revealed slightly different characteristics, such as the rate of nucleation, film resistivity, impurity content, and microstructure. Figure 5 shows the SEM micrographs of Cu films deposited using two different carrier gases, H_2 and Ar. Both were deposited on TiW substrates at a temperature of 200°C and a pressure of 500 mTorr using a carrier gas flow rate of 20 sccm and a deposition time of 10 min. The nucleation rate of Cu with H_2 as the carrier gas was faster than that with Ar as the carrier gas. Table I shows that different carrier gases resulted in different resistivities and deposition rates. The film resistivity was determined by sheet resistance measurement and film thickness measurement, while the deposition rate was determined by averaging the thicknesses of the films deposited with the deposition time. Hydrogen can react with the by-product of the Cu precursor in the following way



$$H_2 + Cu(hfac)_2 \rightarrow 2Hhfac+Cu$$

Thus, the deposition rate of Cu films using H_2 as the carrier gas is faster than using an inner gas such as Ar and N_2. Moreover, since H_2 can react with the residual fragment of precursor, the impurity content in Cu films was reduced significantly. The carrier gas H_2 will not only act as a reducing agent,[13–15] thus leading to an increase in deposition rate, but also react with the residual precursor fragments, thereby leading to reduced impurity contents in Cu films.[13,14] This in turn causes lower resistivity in Cu films. It is obvious that H_2 plays a role of promoter as well as cleanser.[16,17]

Figure 6 shows the TEM micrographs of Cu films deposited using three different carrier gases, H_2, Ar, and N_2. All were deposited on TiW substrates at 200°C and 500 mTorr using a carrier gas flow rate of 100 sccm. Using different carrier gases resulted in Cu films with different microstructures. Copper films deposited using H_2 as a carrier gas have a denser microstructure with smaller grain size, while the Cu films deposited using Ar or N_2 as a carrier gas displayed much bigger grains which appear to be agglomerated from many smaller grains. Figure 7 shows SEM micrographs of Cu films deposited using Ar as a carrier gas, indicating that Cu tended to nucleate on the Cu nuclei. Thus, the big grains shown in Fig. 6b and 6c are likely accumulation of Cu nuclei. From residual gas analysis conducted during deposition, we have found different hydrogen levels depending on the substrate used. We presume that hydrogen may be attracted to the surfaces of conductor substrates from a chemical mechanism, with subsequent

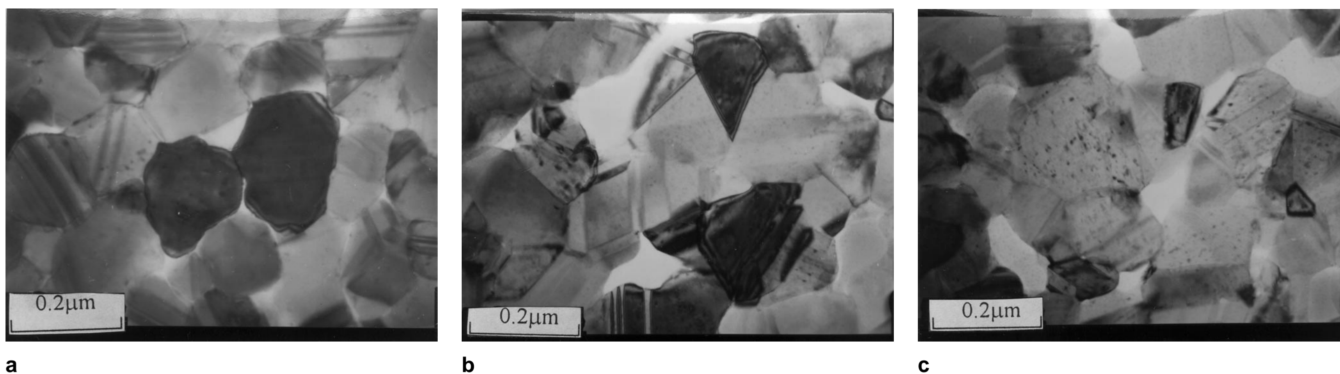


Fig. 6. TEM micrographs of Cu films deposited on TiW at 200°C and 500mTorr with 100sccm carrier gas flow rate of (a) H_2, (b) Ar, and (c) N_2.

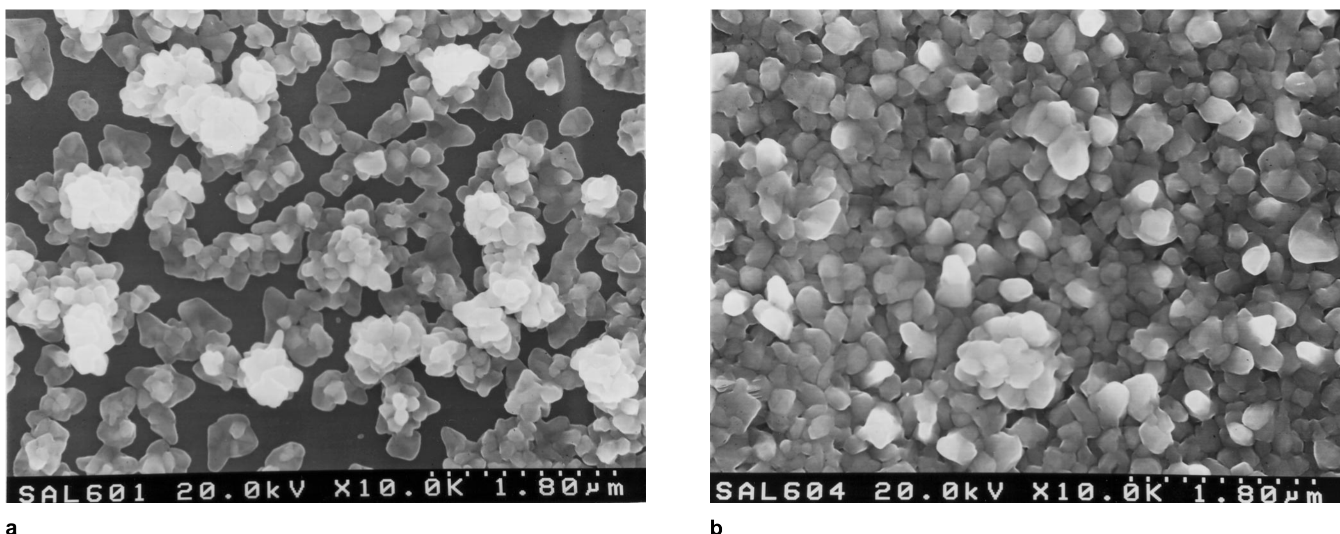


Fig. 7. SEM micrographs of Cu films deposited on TiW at 200°C and 500mTorr with 100 sccm carrier gas flow rate of Ar for a deposition time of (a)5 and (b)10 min.

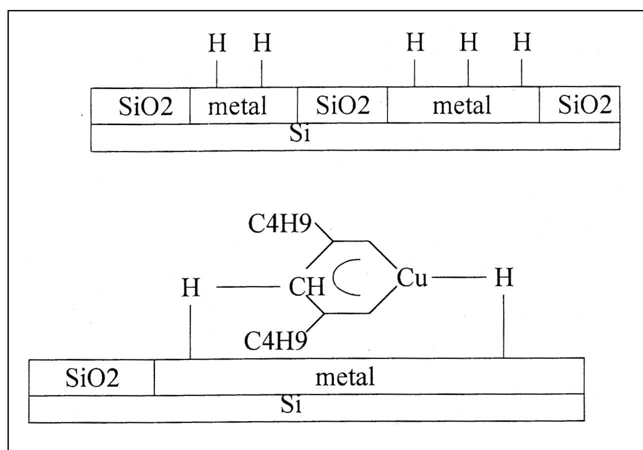


Fig. 8. Effects of hydrogen adsorption on the copper deposition (a) adsorption of hydrogen to the conductor substrate surfaces, and (b) adsorption of precursor to the substrate surfaces through a direct bonding with the surface hydrogen.

chemisorption of the β-diketonate precursor through direct bonding between the surface H and the CH radical in the precursor. This forms CH_2,[18] as illustrated in Fig. 8. The precursor then decomposes, yielding a Cu-H thin layer which proceeds with desorption of the precursor byproducts. The copper layer then grows on this "seed" CuH layer. It is this hydrogen adsorption effect that allows Cu films deposited using H_2 as a carrier gas to have a denser microstructure (Fig. 6). The hydrogen causes formation of denser Cu nuclei on the substrates from the initial nucleation stage (Fig. 5). Without this "seed" Cu-H layer, the preferential nucleation of Cu on the Cu nuclei results in agglomeration, bigger grains, and lower deposition rate as observed when using Ar or N_2 as a carrier gas. In fact, preferential adsorption of hydrogen to conductor substrates, but not to insulator substrates, is the key factor in the selective growth of Cu CVD.[18]

Figure 9 shows the XRD spectrum of a 1 μm thick Cu film deposited on TiW substrate at a pressure of 500 mTorr, indicating a polycrystalline structure. We found from the XRD analysis that all Cu films deposited in this work, regardless of deposition temperature, have a structure of the fcc Bravais lattice. We also found that Cu films deposited at higher temperatures contain a more porous microstrucure. These pores have the effect of increasing the resistivity of Cu films.

Since the substrate surface conditions play an

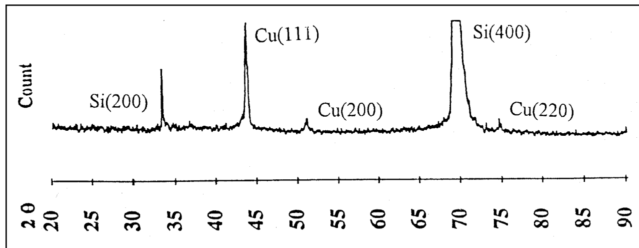


Fig. 9. XRD spectrum of Cu films deposited on TiW substrates.

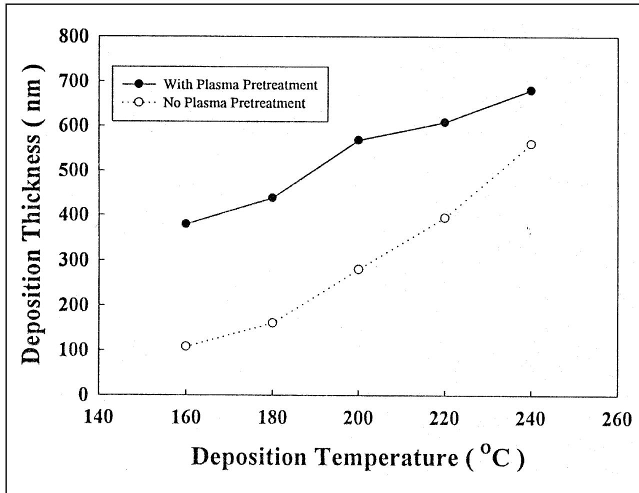


Fig. 10. Cu film thickness as a function of deposition temperature for the TiW substrates with and without N_2 plasma treatment.

important role in CVD of Cu films, it is anticipated that a plasma treatment on the substrate surfaces prior to the Cu deposition should have beneficial effects on the deposition of Cu films.[19] In this work, N_2 plasma was used for substrate surfaces treatment. Figure 10 shows the Cu film thickness as a function of deposition temperature for the TiW substrates with and without N_2 plasma treatment. The N_2 plasma was performed ex situ, in a reactor (ULVAC ERA 1000S) at a power of 100 W with an N_2 flow rate of 80 sccm. It is obvious that the N_2 plasma treatment modified the substrate surfaces, resulting in an increase in nucleation rate and growth of Cu films.

CONCLUSION

The copper chemical vapor deposition (Cu CVD) using Cu(hfac)TMVS as the precursor was investigated. We found that the Cu-CVD using H_2 as a carrier gas resulted in Cu films of the lower resistivity, denser microstructure and faster deposition rates than using Ar or N_2 as the carrier gas. Hydrogen, not only acts as a reduction agent, but also reacts with the residual precursor fragments. Additionally, we found that an N_2 plasma pretreatment of the substrate surface substantially increased the deposition rate of Cu films.

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