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## MATERIAL AND ELECTRICAL CHARACTERISTICS OF COPPER FILMS DEPOSITED BY METAL-ORGANIC CHEMICAL TECHNIQUE NAM-IHN CHO, DONG-IL PARK, AND H. GIN NAM

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### ABSTRACT

Material and electrical characteristics of copper thin films prepared by metal organic chemical vapor deposition (MOCVD) have been investigated for interconnection applications in ultra large scale integration circuits (ULSI). The copper films have been deposited on TiN substrates using a metal organic precursor, hexafluoro acetylacetonate trimethylsilyl copper, VTMS(hfac)Cu (I). Deposition rate, grain size, surface morphology, and electrical resistivity of the copper films have been measured from samples prepared at various experimental conditions, which include substrate temperature, chamber pressure, and carrier gas flow rate. Results of the experiment showed that the electrical property of the copper films is closely related to the crystallinity of the films. Lowest electrical resistivity,  $2.4 \mu\Omega \cdot \text{cm}$  was obtained at the substrate temperature of  $180^\circ\text{C}$ , but the resistivity slightly increased with increasing substrate temperature due to the carbon content along the copper grain boundaries.

### INTRODUCTION

With increasing device density of integrated circuits (IC), there is a demand for a new interconnection technology in IC fabrication processes<sup>1, 2</sup>. Conventional interconnection technology, Al-based sputtering, suffers from low electromigration resistance and bad step coverage<sup>3</sup>. As a result, Al sputtering interconnection scheme will soon become performance limiting. One of the most promising candidates is a copper chemical vapor deposition (Cu-CVD) technology<sup>4-17</sup>. It has lower resistivity than that of Al alloys and has exhibited resistance to electromigration. Also, Cu-CVD has been expected to have better step coverage characteristics. However, copper diffuses easily in silicon, and dry etching

of copper requires a high temperature. This study is to investigate material and electrical properties of copper thin films prepared by chemical vapor deposition with a metal organic precursor at relatively low temperatures<sup>18-21</sup>. In this paper, we present the applicability of the films to the sub-quarter-micron device fabrications as the interconnection material.

### PREPARATION OF COPPER FILMS

The experimental system used in this study is shown in Fig. 1. The system consists of a gas feeding system, a reaction system, and an exhaust system. The reaction chamber was evacuated by turbo molecular pump, and the base pressure of the chamber was in the

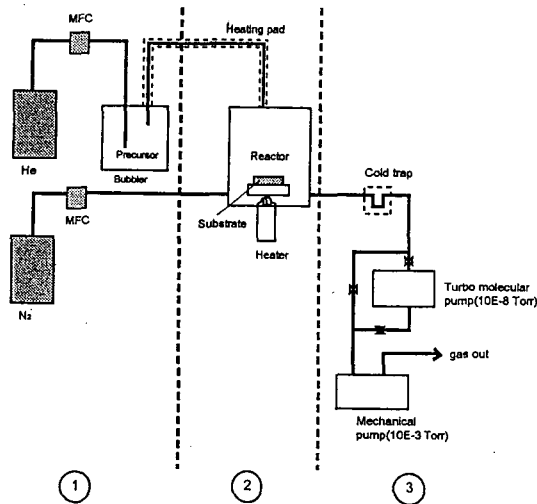
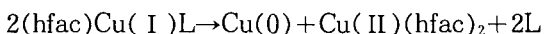


Fig. 1. Schematic diagram of copper film deposition system.

range of  $10^{-6}$  Torr. Precursor of thin copper deposition was a metal organic compound, named (hfac)Cu(I) VTMS (hexafluoroacetylac-

tonate trimethylvinylsilane copper). The compound is known to deposit pure copper by a disproportionation reaction in which two copper (I) species react to form a copper (II) compound and a copper atom<sup>22)</sup>. The reaction mechanism of the copper deposition can be presented by following chemical relation,



where L is the Lewis base ligand, including VTMS ( $=\text{CH}_2\text{CHSiMe}_3$  and hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate. The Cu(I) precursor has been used in many studies, since it provides higher vapor pressure than Cu(II) organics<sup>23)</sup>. The chemical structure of the precursor is shown in Fig. 2<sup>22)</sup>. The precursor was in a bubbler with a 55°C, and the vapor was moved to the reaction chamber by bubbling a carrier gas with the flow rate of 0

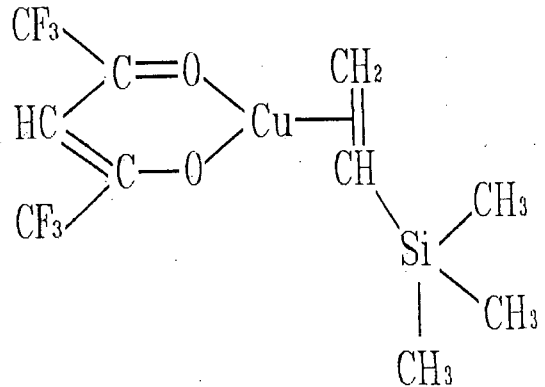


Fig. 2. Chemical structure of (hfac)Cu(I) VTMS precursor.

~200sccm. Helium was used as the carrier gas. The distance between the showerhead of the carrier gas and the substrate was fixed to 3 cm. During the film deposition, the chamber pressure and the substrate temperature were controlled by using the flow rate of the carrier gas and the substrate heater.

Before the deposition of copper films, 200 nm-thick titanium nitride (TiN) films were deposited onto the (100) silicon wafer. The TiN is known to be a diffusion barrier material for Cu atoms. The TiN substrate temperature was varied from 140°C to 250°C, whereas the reaction chamber pressure was varied from 0.3 Torr to 1.0 Torr. After the film deposition, the substrate was cooled down to the room temperature, and purged with nitrogen gas.

## RESULTS AND DISCUSSION

Copper thin films were deposited by a metal organic chemical technique onto TiN substrate with the substrate temperature varying from 140°C to 250°C. The thicknesses of copper films were measured by the  $\alpha$ -step method. The film deposition rate as a

function of substrate temperature is shown in Fig. 3. The deposition rate is shown to be largely increased with increasing substrate temperature, from about 500 Å/min. at the substrate temperature of 140°C to about 2000 Å/min at 220°C. These rates are approximately 200% higher than that obtained in other study<sup>20</sup>, in which they used argon as a carrier gas. In fact, the chemical reaction of the copper deposition is carried out in the atmosphere of the carrier gas and the vapor of the copper organic compound, and thus the chemical reaction speed is determined by the concentration of copper atoms around the substrate. Since the size and the mass of helium is much smaller than those of argon, and the diffusion velocity of Cu in helium is much faster than that of Cu in argon. We may conclude that the deposition rate of Cu film can be increased using helium as the carrier gas. Although the deposition rate is high, the surface roughness measured by AFM (atomic force microscopy) was less than 20 nm when 500 nm-thick copper film was deposited. This characteristic of the surface roughness can

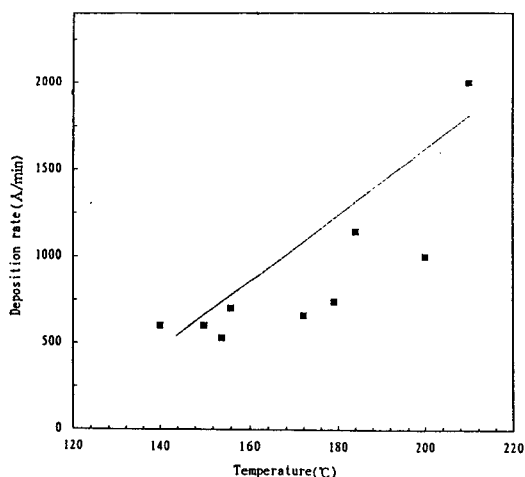
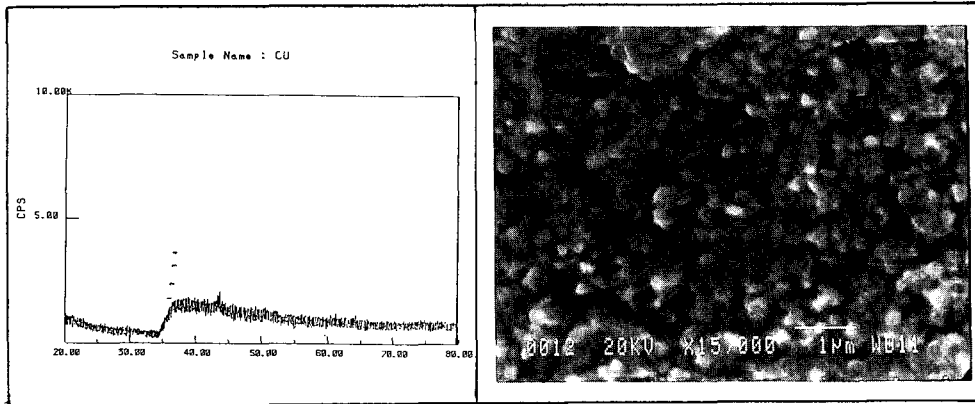


Fig. 3. Growth rate of copper films *vs.* substrate temperatures.

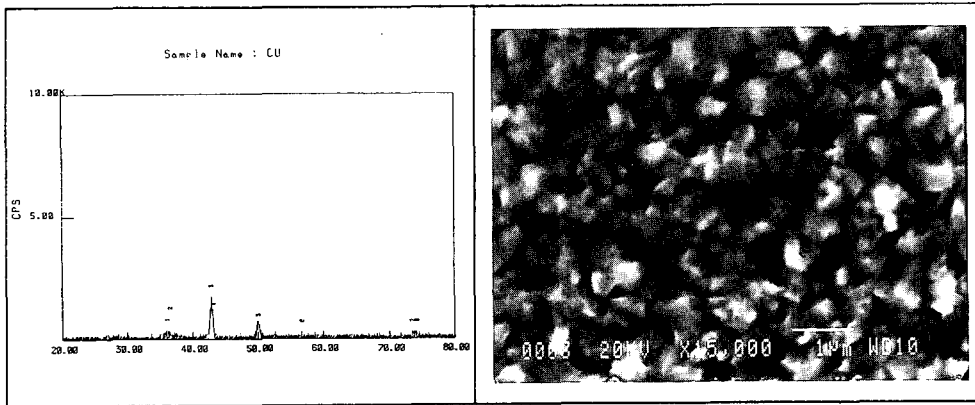
be applicable to the sub-quarter-micron device fabrication, since the requirement for the surface roughness of interconnection material in the IC process is 5% at 500 nm thickness.

Fig. 4 shows SEM (scanning electron microscopy) morphology and XRD (X-ray diffraction) pattern of Cu films prepared at three different substrate temperatures. The SEM system was JEOL model JSM-840A. The acceleration voltage was set at 10keV, and the magnification was 15,000. Higher substrate temperature during the Cu deposition apparently increases the grain size and the crystallinity of the copper films. For samples which was deposited with substrate temperature of 150°C, the grain size of the Cu film was less than 0.2 $\mu$ m, and the XRD pattern of Cu film showed mixed structures of polycrystalline and amorphous phases. When the substrate temperature was increased to 200°C, the Cu films changed their structures to polycrystalline phases, and the grain size became about 0.8 $\mu$ m. When the reaction temperature reached 250°C, the Cu grain size was measured to be about 1.2 $\mu$ m, and the grains were closely packed.

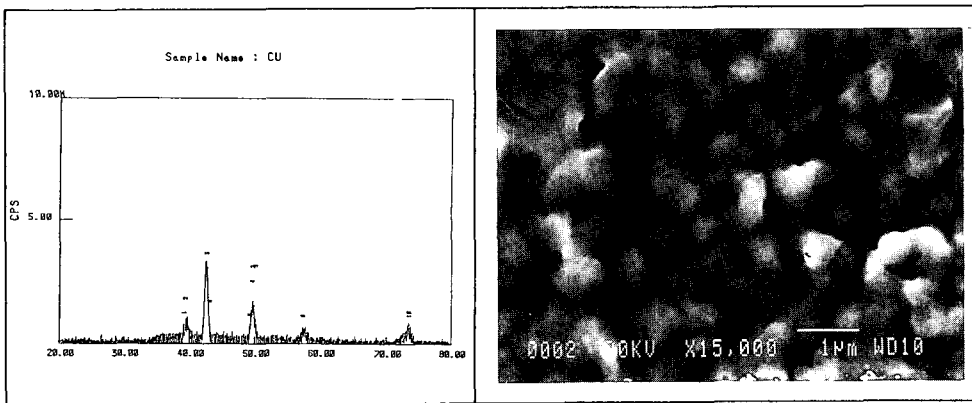
Variations of electrical resistivity of the Cu films with the substrate temperature, measured by 4-point probe method, ranged from near 6.5 $\mu\Omega \cdot$ cm at 150°C to as low as 2.4 $\mu\Omega \cdot$ cm at 180°C. However, the resistivity of the film was increased above 180°C, even though the grain size was linearly increased with increasing temperature. This trend is shown in Fig. 5. Two possible causes of the high resistivity above 180°C were considered, namely, a carbon contamination and a loose packing of the Cu grains. Any loose packing of Cu grains were observed in SEM morphol-



(a)



(b)



(c)

Fig. 4. SEM morphology and XRD nature of Cu films with different substrate temperatures of (a) 150°C (b) 200°C (c) 250°C

ogy as shown in Fig. 4. In AES (Auger Electron Spectroscopy) analysis as shown in Fig. 6, a small amount of carbon content was detected for the sample prepared at the substrate temperature of 250°C. This is possible

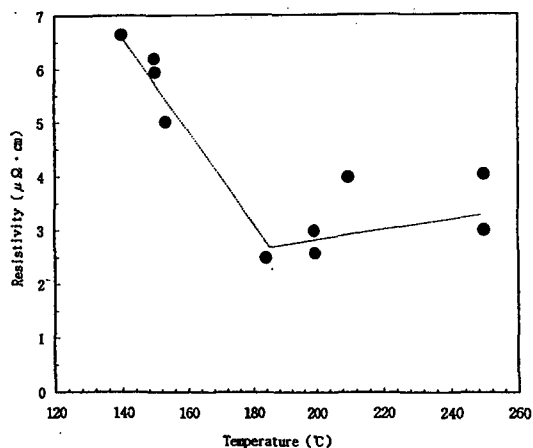
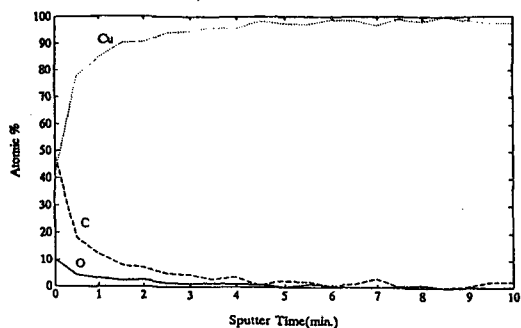
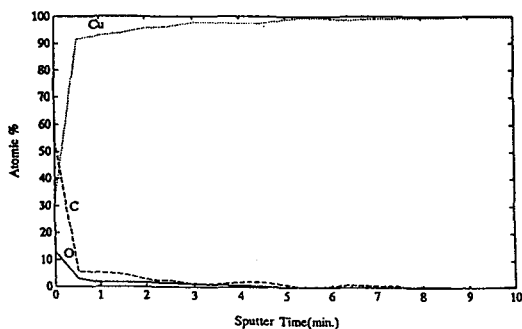


Fig. 5. Electrical resistivity of Cu films vs substrate temperatures.



(a)



(b)

Fig. 6. Auger depth profile for Cu films with substrate temperatures of  
 (a) 150°C (b) 250°C

because the precursor we used contains carbon atoms, and small portion of carbon atoms are chemically reacted with the substrate at higher temperature above 200°C. The carbon content may be located in the Cu grain boundaries, and consequently it increases the resistivity of the films.

The electrical resistivity of the interconnection materials in the sub-quarter-micron IC requires below  $3.0 \mu\Omega \cdot \text{cm}$ , and thus the copper polycrystalline films obtained in this experiment is considered to be suitable as the interconnection materials.

### CONCLUSION

Copper thin films were deposited by metal organic chemical technique onto the TiN substrates, and material and electrical properties of the films were measured. Precursor we used in this study was (hfac)Cu (I)VTMS, and the bubbler temperature was fixed at 55°C. Since we used helium as the carrier gas, higher deposition rate was obtained up to 2,000 Å/min., compared to the previous studies. This result implies that the diffusivity of Cu in helium gas is much higher than that in argon gas. The electrical resistivity of the film was a strong function of substrate temperature. Lowest resistivity of the film was obtain at the substrate temperature of 180°C, but higher substrate temperature over 180°C increased the film resistivity. Auger analysis indicated that higher reaction temperature increased the carbon content of the film and consequently the resistivity of the film. Best results were obtained at the substrate temperature of 180°C and the chamber pressure of 0.8 Torr. With these deposition conditions, the Cu films have the properties of the growth rate of 1200 Å/min, the electrical resistivity of  $2.4 \mu\Omega \cdot \text{cm}$ , and the surface

roughness of less than 5%. These properties are applicable to the interconnection materials of the sub-quarter-micron device fabrications.

### ACKNOWLEDGMENTS

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