

Chapter 2

Sciences in Micro- and Nanoelectronics

Processes Using an Environmentally-Friendly Medium

E. Kondoh, M. Watanabe, Y. Takeuchi, T. Ueno, and M. Matsubara

Abstract Cu thin films were deposited inside micro-sized true three-dimensional high-aspect-ratio through-holes formed in a glass substrate. The deposition was carried out in a supercritical CO₂ solution from a Cu complex via hydrogen reduction to perform conformal coating. The deposition depth, or coating length, increased with decreasing the deposition temperature in straight through-holes. In crank-shaped and Y-shaped holes, Cu thin films with a constant thickness were formed on the sidewalls.

Keywords Supercritical fluids • Carbon dioxide • Thin films • Copper • Interconnect

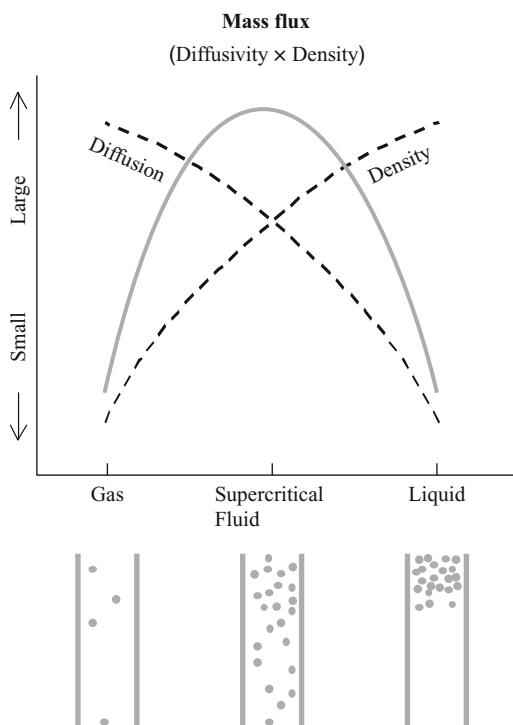
2.1 Introduction

Cu thin film deposition in high-aspect-ratio (HAR) through-holes is a key issue in fabricating new generation through-silicon vias (TSVs) and through-glass vias (TGVs) for 3D chip stacking. Flexible chip design will require complex through-hole interconnections instead of traditional through-holes perpendicular to the substrate surface [1].

Supercritical CO₂ is a high density and environmentally friendly medium. Supercritical CO₂ behaves as both a gas and a liquid and has many unique properties, such as nanopenetration capability, high diffusivity, recyclability, safeness and a solvent ability. A differentiative and distinct property of supercritical CO₂ against vacuum and

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Fig. 2.1 Comparison of diffusion flux of different media



wet processes is its diffusion transport ability. Supercritical CO_2 fluids have a medium diffusivity and medium density, and therefore have a higher diffusion flux than gases or liquids (Fig. 2.1). These are ideal properties for micro and nano fabrication.

Both diffusivity and density of supercritical CO_2 are tunable as functions of pressure and temperature; this means that the fabrication process using supercritical fluids can be adopted to various size scales, from nm to mm scales, leading to simplification and cost reduction in microelectronic fabrication.

In the present study, we demonstrate the use of supercritical CO_2 to deposit a conformal Cu thin film inside micro-sized true three-dimensional (3D) through-holes of various complex shapes. It has been demonstrated that supercritical fluid deposition techniques are capable of filling nanometer-sized features with metals [2, 3].

2.2 Experimental Procedures

Figure 2.2 shows a schematic illustration of the flow-type reaction system used in the present study. $\text{Cu}(\text{dibm})_2$ was used as a Cu source and dissolved in acetone. The solution was then injected into the supercritical CO_2 fluid, which was then

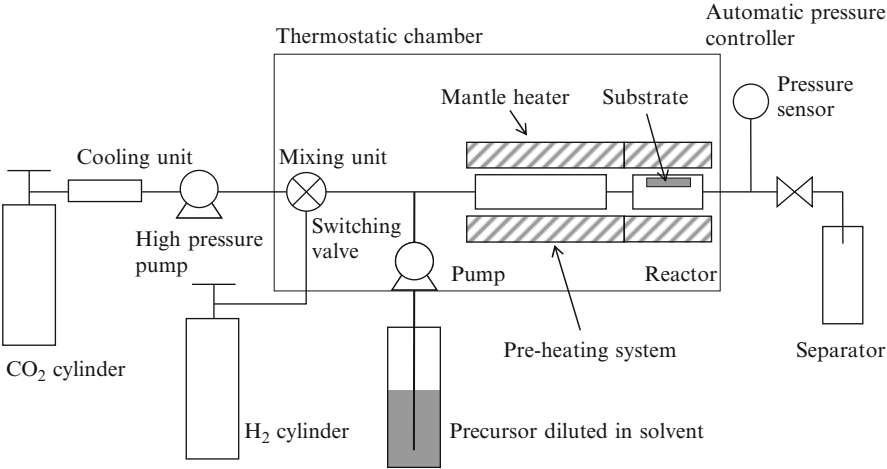


Fig. 2.2 Schematic illustration of a flow-type reaction system

Table 2.1 Deposition conditions	Deposition temperature (K)	493–553
	Pressure (MPa)	10
	Deposition time (min)	60, 240, 480
	CO ₂ flow rate (mol/min)	77.5×10^{-3}
	H ₂ concentration (mol%)	1.53
	Cu(dibm) ₂ concentration (mol%)	29.2×10^{-3}
	Acetone concentration (%)	5.2 (in CO ₂)

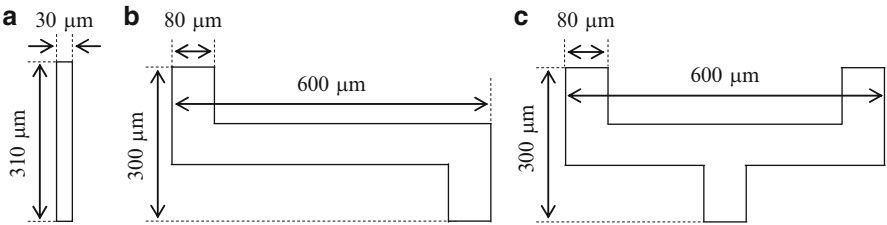


Fig. 2.3 Schematic diagrams of the shapes of through-holes. (a) Straight, (b) crank-shaped, (c) Y-shaped

preheated to 423 K and supplied to a reactor placed in a heating mantle. The substrate was fixed facedown on the reactor wall.

The deposition conditions are summarized in Table 2.1. The substrate was a glass plate containing through-holes of various shapes as shown in Fig. 2.3. After deposition, cross-sections of the samples were examined using optical microscopy and scanning electron microscopy.

2.3 Results and Discussion

Figure 2.4 shows cross-sectional images of Cu thin films deposited in straight through-holes at different deposition temperatures. The deposition of the Cu thin films occurred on the surfaces of the glass substrate and the sidewalls of the through-holes at temperatures between 493 and 553 K. The deposition depth increased with decreasing deposition temperature. At a lower temperature (Fig. 2.4a), the thickness of the Cu thin film was almost constant over the through-hole sidewall. At a higher temperature (Fig. 2.4b), the Cu thin films were formed from the top of the hole to a depth of approximately 150 μm . These tendencies indicate that the Cu precursor was consumed at the top of the hole when the temperature was high. However, at a lower temperature, the Cu precursor reached the bottom of the hole because low consumption of the precursor allowed good diffusion transport of the precursor.

Figure 2.5 shows top view transmission optical micrographs of the crank-shaped and Y-shaped through-holes after Cu deposition. Compared with the samples before deposition, it is obvious that the light was not transmitted through the

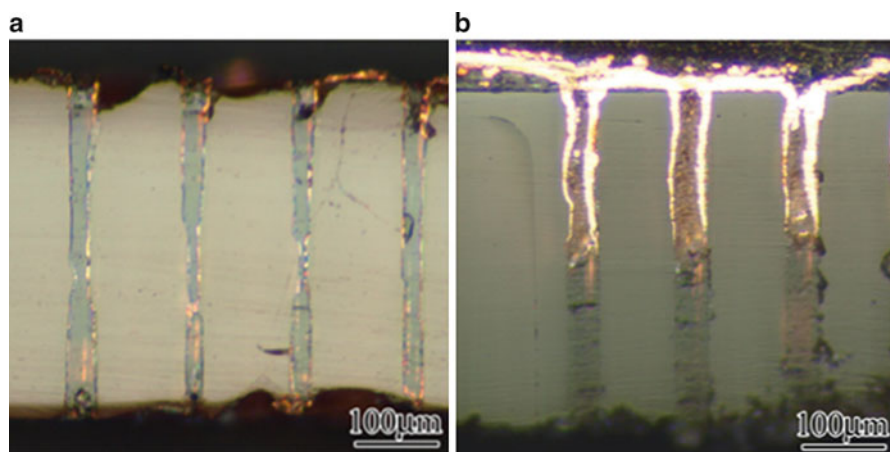


Fig. 2.4 Cross-sectional images of the straight through-holes lined with Cu thin films. Deposition temperature of (a) 493 K and (b) 553 K

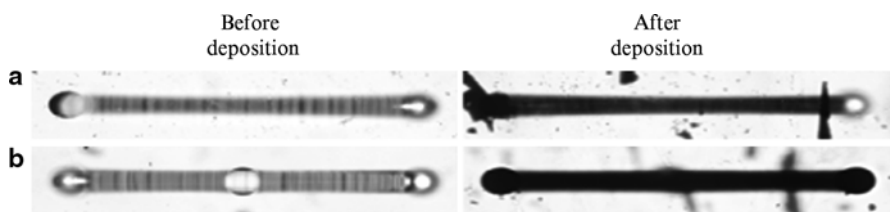


Fig. 2.5 Top-view transmission optical micrographs of (a) crank-shaped and (b) Y-shaped through-holes

holes. This indicates that the Cu thin films completely coated the surface of the through-holes. Cross sectional SEM images (not shown) of a crank-shaped through-hole exhibited that the thickness of the Cu thin film formed inside the hole was similar to the thickness of the Cu film formed on the glass plate surface (205 nm). These findings were the same for the Y-shaped through-hole. These thickness distributions cannot be explained by diffusion transport behavior alone. Numerical fluid flow dynamics simulations are currently being carried out and will be presented in the nearest future.

2.4 Conclusions

Cu thin films were successfully deposited on the sidewalls of micro-sized straight, crank-shaped, and Y-shaped through-holes opened in glass substrates. The thickness of the Cu thin films formed inside the holes was similar to that formed on the glass plate surfaces. The mechanism of deep coating was discussed in relation to the transport of the Cu precursor.

References

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