

# Paving the way for Full-Fluid IC Metallization using Supercritical Carbon Dioxide

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## Abstract

Metal thin films for IC metallization are currently deposited either from vapor (PVD/CVD) or liquid (e.g. ECD). This paper reports critical bases for full IC metallization using only supercritical carbon dioxide (scCO<sub>2</sub>) fluids as a deposition medium. High-aspect-ratio filling capability, (111)-preferential growth, low temperature deposition possibility, important roles of solvent capability of scCO<sub>2</sub> including F-less solid precursor utilization, and barrier metal deposition possibility are described.

## Introduction

Supercritical CO<sub>2</sub>, the critical point of which is 7.4MPa and 31°C, has been so far successfully utilized in chemical processing, and is now of considerable interest in applying to IC processing. In the supercritical state CO<sub>2</sub> has a molecular number density as high as that of liquids and diffusivity as high as that of gases. ScCO<sub>2</sub> can thus penetrate deep into small features and deliver Cu precursors with a high mass flux. Conversion of the precursors to metallic Cu in the scCO<sub>2</sub> realizes Cu filling in high-aspect-ratio small features at a high deposition rate. This meets the requirements not only for further downscaling to nano size but also for the fabrication of inter-chip conductors of 3D ICs where deci-micron deep features are involved.

Metal deposition in supercritical fluids from metal-organic precursors has been reported [1,2]. Recently, it was demonstrated that the scCO<sub>2</sub> fluid deposition is capable of filling metals into deci-nanometer small features [3]. This work has independently started [4], stimulated by the progress of R&D of scCO<sub>2</sub> in LSI manufacturing. The concept of the Cu deposition in scCO<sub>2</sub> is shown in Fig. 1.

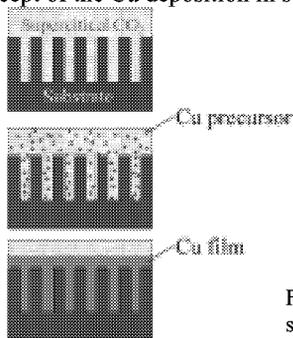


Fig. 1 Process concept of scCO<sub>2</sub> deposition

In this work Cu deposition from Cu<sup>II</sup> and Cu<sup>I</sup> precursors is investigated. Basic film characterization, demonstration of narrow feature filling capability, and barrier metal deposition possibility are also studied.

## Deposition Method

Carbon dioxide, a metal precursor, and H<sub>2</sub>, if needed, were introduced into a high-pressure reactor. The liquid CO<sub>2</sub> was pumped using a plunger pump to attain a pressure above the critical point of CO<sub>2</sub>. The pressures and temperatures were 10-15MPa and 180-400°C, respectively. A typical molar ratio of H<sub>2</sub> to the precursor was about 10 [4].

## Results and Discussion

### Basic deposition characteristics: Deposition through Cu<sup>II</sup>(hfac)<sub>2</sub>-H<sub>2</sub> chemistry

In the Cu<sup>II</sup> chemistry, addition of H<sub>2</sub> was essential. The deposits obtained from Cu(hfac)<sub>2</sub> (hfac = hexafluoroacetylacetonate) without H<sub>2</sub> were reddish-brown and rather granular. XRD and XPS nevertheless showed the presence of crystalline and metallic Cu. A significant improvement of the film quality is observed when H<sub>2</sub> was added. The quality improvement stated here involves the appearance of metallic shiny copper color, the formation of a continuous film structure, an increase in deposition yield, and good experimental reproducibility.

A preferential growth on conductive substances, e.g. on Fe, Au, Cu, WN, TiN, TaN, and HF-treated p-Si was observed. Shiny and continuous films were formed on the metals, whereas on the p-Si that received a laboratory-level HF-treatment the film exhibited a less shiny and continuous feature. Such effects of the H<sub>2</sub> addition are similar to the ones reported for chemical vapor deposition [5]. This similarity suggests that the surface dissociation of H<sub>2</sub> is involved in the deposition mechanism presumably as the rate-determining step.

The deposition rates obtained were 30–50 nm/min. These values are practically sufficient at sub-100mm technology nodes. A further increase would be achieved by increasing the precursor concentration. The yield of Cu was excellently high, reaching almost 100% when a closed vessel, or a batch type reactor, was used. This high yield makes scCO<sub>2</sub> deposition very attractive against Cu CVD; in the latter most of the Cu source is exhausted and wasted.

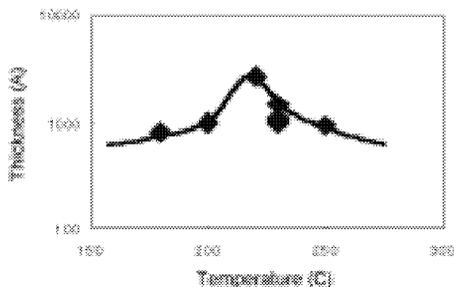


Fig. 2 Temperature dependence of Cu film thickness.

Figure 2 shows the temperature dependence of Cu film thickness. The precursor concentration was much lowered compared to the above-mentioned case so as to carry out more precise experiments. The deposition time was 15 min. It is seen that the deposition rate has a maximum at around 220°C. This temperature is much lower than typical Cu CVD temperatures using  $\text{Cu}(\text{hfac})_2$  [5,6]. It is noted that practically no deposition was observed above 350°C.

Figure 3 shows XPS depth profiling of a deposited Cu film. Practically no carbon, oxygen, and fluorine impurities are found in the film. In the XRD spectrum shown in Fig. 4 the (111) peak at 43° is predominant, which indicates the preferential growth of (111) faces parallel to the substrate.

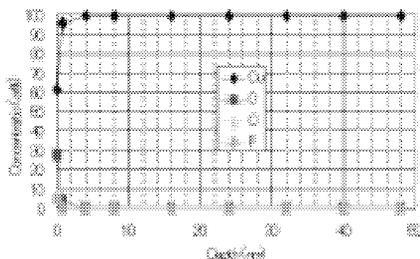


Fig. 3 XPS depth profiling of a Cu film deposited from  $\text{Cu}(\text{hfac})_2$ .

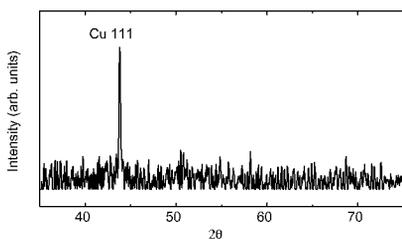


Fig. 4 XRD patterns of Cu films deposited using  $\text{Cu}(\text{hfac})_2$ .

The reflectivity in the visible-wavelength range (350–800nm) was measured for a 3000Å-thick film. The measured reflectivity was about 90–95% of that of an unpatterned sputtered film (Fig. 5). The spectrum showed no cutoff wavelength, indicating a flat surface topography. This is speculated to be due to a high number density of the precursor thus to a high nucleation density. The resistivity of a 4000Å-thick Cu film obtained at 230°C was 2.15  $\mu\Omega\cdot\text{cm}$  (as-deposited).

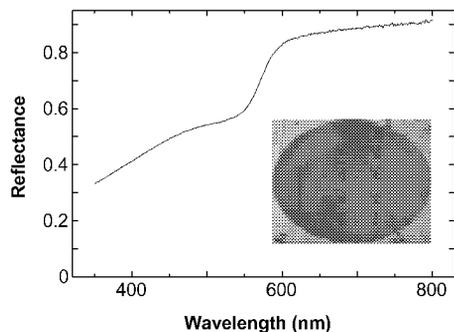


Fig. 5 Reflectance spectrum of a 3000Å-thick Cu film. Inset: Appearance of a Cu film deposited on a single wafer using a student-built deposition tool.

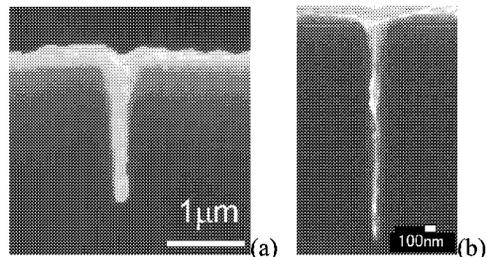


Fig. 6 Trial filling in narrow features using (a)  $\text{Cu}(\text{hfac})_2$  and (b)  $\text{Cu}(\text{dibm})_2$ .

Figure 6 shows cross-sectional electron micrographs taken after a trial Cu filling into sub100–150nm-at-bottom features. Although still being far away from optimization, a good filling capability was demonstrated.

#### Use of fluorine-less $\text{Cu}(\text{dibm})_2$ - $\text{H}_2$ chemistry

Deposition using F-less  $\text{Cu}(\text{dibm})_2$  (dibm = diisobutylmethanate) resulted in very similar results. Figure 6b demonstrates a good filling capability as the case of  $\text{Cu}(\text{hfac})_2$ . Compared to  $\text{Cu}(\text{hfac})_2$ , films deposited  $\text{Cu}(\text{dibm})_2$  generally showed a better adhesion. We presume that the absence of F in the deposition chemistry strengthened the Cu/substrate interface. Since F-less precursors having a high vapor pressure are hardly synthesized,  $\text{scCO}_2$  deposition technology is to be an ideal way to utilize low volatile precursors that have not been solely applied to CVD metallization.

#### Deposition through $\text{Cu}^I$ chemistry with no $\text{H}_2$

Copper deposition from  $\text{Cu}^I(\text{hfac})\text{L}$  (L = aryloxytrimethylsilyl), a liquid precursor originally developed for Cu CVD, through a disproportionation reaction,  $2\text{Cu}(\text{hfac})\text{L} \rightarrow 2\text{Cu}(\text{hfac}) + 2\text{L} \rightarrow \text{Cu} + \text{Cu}(\text{hfac})_2$ , was successfully carried out. It should be stressed that this reaction does not require a reduction agent. Compared to the  $\text{Cu}(\text{hfac})_2$ - $\text{H}_2$  chemistry the deposition reaction seemed to largely depend on temperature and mass transport. Figure 7 left shows a surface SE micrograph of a deposited Cu film. The AES

depth profiling (Fig. 7 right) shows that common impurities are under the background level

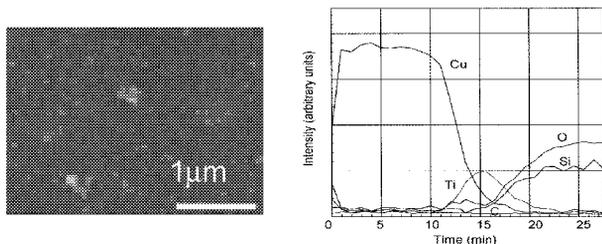


Fig. 7 Surface topography of a Cu film deposited from Cu(hfac)L on TiN/SiO<sub>2</sub> without H<sub>2</sub> (left). The AES depth profiling (right) proves the success of Cu deposition using this chemistry. The impurity signals in Cu are under the background level.

### Critical roles of the solvent capability of scCO<sub>2</sub>

As described above, the capability of scCO<sub>2</sub> to solve low-volatile solid precursors is a primacy of this technique over common CVD techniques. However, in view of deposition chemistry itself, there is a natural question arising, i.e., ‘Is deposition in scCO<sub>2</sub> the same as mega-pressure (ultra-high-pressure) CVD?’ In order to address this question, deposition was carried out with using Ar ( $T_c = 150.7\text{K}$  and  $P_c = 4.86\text{MPa}$ ).

The scAr + H<sub>2</sub> deposition resulted in a poor film surface topography (Fig. 8 right) and in a higher impurity content. This result demonstrates that the solvent capability of scCO<sub>2</sub>—its presence is the primary difference between scCO<sub>2</sub> and scAr—plays an important role in the deposition chemistry. It is presumed that the solvent capability increases the out-going byproduct flux as well as precursor incident flux. The former should have a striking influence on the film quality otherwise the byproducts tend to reside at/near the growing surface and to deteriorate the film quality. ScCO<sub>2</sub> deposition is thus a potentially clean- and high-quality process. The decrease in deposition temperature compared to CVD is also thought to be a consequence of the solvent capability.

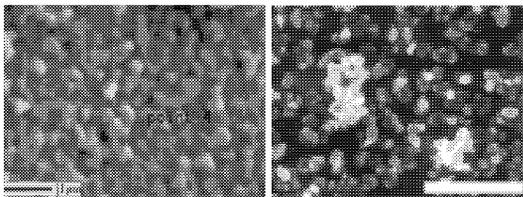


Fig. 8 Surface topography of Cu films deposited with scCO<sub>2</sub> + H<sub>2</sub> (left) and scAr + H<sub>2</sub> (right). The scale bars show one micron.

### Barrier metal deposition possibility

A key to full-supercritical fluid metallization is barrier metal deposition. We are now investigating Ta film deposition in a supercritical fluid. The Auger electron spectrum shown in Fig. 9 is the first evidence of Ta film

deposition where a solid compound of Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub> was used as a source precursor. The deposition temperature was ca 350°C, and H<sub>2</sub> was added to obtain a continuous deposit. Although the film still contains impurities such as C and O, this clearly demonstrates that scCO<sub>2</sub> deposition can be extendable to vacuum-free ‘full-fluid’ metallization.

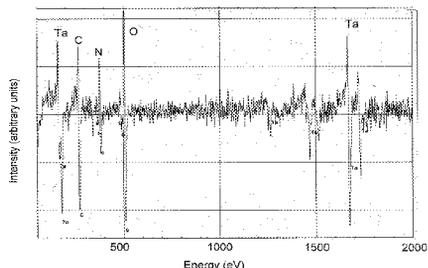


Fig. 9 Auger electron spectrum of a Ta film deposited using Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub> + H<sub>2</sub>.

### Conclusions

Cu was deposited in supercritical CO<sub>2</sub> from Cu<sup>II</sup> and Cu<sup>I</sup> precursors. High-aspect-ratio filling capability, (111)-preferential growth,  $\rho = 2.15 \mu\Omega\cdot\text{cm}$  (as-depo), low temperature deposition possibility, important roles of solvent capability of scCO<sub>2</sub> including the utilization of a F-less solid precursor, and barrier metal deposition possibility were described. The solvent capability of scCO<sub>2</sub> is thought to provide unique features such as the utilization and recycling of low-volatile solid precursors, deposition temperature lowering, and film quality improvement. The possibility of Ta deposition was firstly reported. In conclusion, the supercritical fluid chemical deposition is of a promising replacement of chemical vapor and electro/electroless deposition and of an environmentally friendly low-cost process.

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