

# Deposition of Cu thin films from supercritical carbon dioxide using hexafluoroacetylacetonatecopper

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## Abstract

Common deposition techniques for the metallization of ultra-large scale integrated circuits utilizes vapor (physical/chemical vapor deposition) or liquid (e.g. electro-chemical deposition). This paper reports the use of supercritical CO<sub>2</sub> fluids as a new medium for depositing Cu thin films, where Cu is grown from a metalorganic precursor dissolved in the fluid. Hexafluoroacetylacetonatecopper (Cu<sup>II</sup> (hfac)<sub>2</sub>) was used as the precursor, and depositions were carried out at pressures of 10–15 MPa and temperatures of 180–400 °C. We observed preferential growth of Cu on conductive substrates, a lower deposition temperature of 180 °C by about 100 °C than typical values reported for Cu chemical vapor deposition from Cu<sup>II</sup> (hfac)<sub>2</sub>. The temperature dependence of the deposition rate was further studied and the activation energy for the growth was determined at 0.42 ± 0.12 eV. Basic film characterization was also performed; X-ray photoelectron spectra of the films showed pronounced metallic Cu peaks and trace level of impurity elements, and X-ray diffractometry showed (111) film texturing. Copper filling into nano high-aspect-ratio features was also demonstrated. Finally, a critical role of the solvent capability of supercritical CO<sub>2</sub> on the film quality was discussed with comparative depositions using supercritical Ar.

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## 1. Introduction

Supercritical carbon dioxide (scCO<sub>2</sub>) fluid, of which critical point is 7.38 MPa and 31.0 °C[1], has a molecular density as high as that of liquids, a high diffusivity and low viscosity as those of gases, zero surface tension, and solvent capability. In addition, scCO<sub>2</sub> is a stable, non-toxic, affordable, and recyclable medium. Because of these unique characteristics, scCO<sub>2</sub> has been successfully utilized in food processing and chemical engineering. Considerable attention is now paid to using scCO<sub>2</sub> for semiconductor processing from wafer cleaning, photoresist-stripping, photoresist drying, and to manufacturing porous low-dielectric-constant thin films[2,3].

The idea of the present work is to use scCO<sub>2</sub> as a reaction medium for Cu thin film deposition. In this technique, a metalorganic Cu precursor is dissolved in the scCO<sub>2</sub>, and the deposition reaction proceeds in the scCO<sub>2</sub> environment itself. Due to its high diffusivity and zero surface tension, scCO<sub>2</sub> penetrates deep into high-aspect-ratio (HAR) features and thus deliver the metal organic precursor. By applying a proper reaction chemistry, such small features as via holes in ultra-large scale integrated circuits (ULSIs) can be filled with Cu. In addition, scCO<sub>2</sub> has a high density and compressivity, so that its molecular number density can be widely controlled as functions of pressure and temperature. This controllability affords a possibility of controlling the deposition rate in a wide range, compared to conventional deposition techniques but with keeping good gap-filling capability. This property is very attractive in view of metallizing HAR topographies such as ULSI nano interconnects, bridging via three-dimensional integrated circuits, and microelectromechanical components.

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A known deposition method using supercritical fluid is so-called rapid expansion of supercritical solution [4]. This method basically uses supercritical fluids as a carrier medium of a metalorganic precursor for chemical vapor deposition (CVD), or an analogous manner, where the fluid is delivered to the deposition chamber being maintained at a reduced or atmospheric pressure. A few papers have been published regarding the fabrication of continuous thin films in supercritical fluids themselves [5,6]. Recently it was reported that the metal deposition technique in  $\text{scCO}_2$  is capable of filling HAR features ULSI via holes [7,8]. The present work has been originally and independently started from the author's background in metalorganic chemical vapor deposition [9,10]. In view of its novelty, potential impact to the future ULSI technology, but lack of publication, more work is obviously needed. Indeed, many research subjects are still being enrolled, covering from the deposition science, to understanding practical advantages/limitations against the existing deposition methods, and to the realization of ULSI interconnect processing.

In this article, deposition characteristics from  $\text{scCO}_2$  using hexafluoroacetylacetonatecopper ( $\text{Cu}(\text{C}_5\text{HF}_6\text{O}_2)_2$ , abbr.  $\text{Cu}(\text{hfac})_2$ ) is reported.  $\text{Cu}(\text{hfac})_2$  was chosen as the precursor because of its easiness in handling, long shelf life, high vapor pressure, and the availability of many past publications on Cu CVD.

## 2. Experimental details

Fig. 1 is a schematic diagram of the apparatus used in this work. Liquid  $\text{CO}_2$  was supplied from a usual siphon cylinder and was further liquefied using a cooling unit. The  $\text{CO}_2$  was then pumped into a stainless steel-made high pressure reactor, directly or after passing through the precursor reservoir (see below). The volume of the reactor

and the reservoir was  $2.2 \text{ mm}^3$  and  $5.0 \text{ mm}^3$ , respectively. The reactor was heated with a convection furnace or heating mantle at above the critical point. The reactor temperature was measured with a thermocouple inserted in a small hole drilled in the reactor wall.

Two different arrangements for the precursor supply were employed in the present work; so-called static and semi-dynamic arrangements. In the static arrangement,  $\text{Cu}(\text{hfac})_2$  and  $\text{H}_2$  were filled together with a substrate in the reactor usually prior to pumping  $\text{CO}_2$ . After supplying  $\text{CO}_2$ , the reactor was introduced in the isothermal region of the convection furnace maintained at an operating temperature. There was indeed an observed temperature difference between the furnace and reactor. The effect of the temperature difference is discussed along with the experimental data. The volumetric amount of  $\text{Cu}(\text{hfac})_2$  was fixed at  $2.95 \times 10^{-3} \text{ mol/cm}^3$  and the  $\text{H}_2/\text{Cu}(\text{hfac})_2$  molar ratio was about 10.

As for the semi-dynamic arrangement, the  $\text{Cu}(\text{hfac})_2$  was dissolved in the reservoir at 13 MPa and  $80^\circ\text{C}$  (above the critical point) so as to form a  $\text{Cu}(\text{hfac})_2 + \text{scCO}_2$  solution. The solution was then pumped to the reactor being priorly filled with  $\text{H}_2$  and kept at a constant temperature using the heating mantle. In this arrangement, the temperature difference during deposition between the reactor and heater was below  $1^\circ\text{C}$ . The amount of  $\text{Cu}(\text{hfac})_2$  was  $1.5 \times 10^{-5} \text{ mol/cm}^3$  of the reservoir.

The pressures and heater temperatures for deposition were 10–15 MPa and  $180\text{--}400^\circ\text{C}$  in each case. The data described in this paper were obtained using the static arrangement unless otherwise stated. The bifurcation of the two arrangements are described in the text.

Wafers used were bare Si(100),  $\text{SiO}_2/\text{Si}$  coated with refractory metal films (TaN, TiN, WN), and hole/trench-patterned wafer coupons coated with TiN or WN. Some of the specimens were further coated with 5–20 nm-thick Au

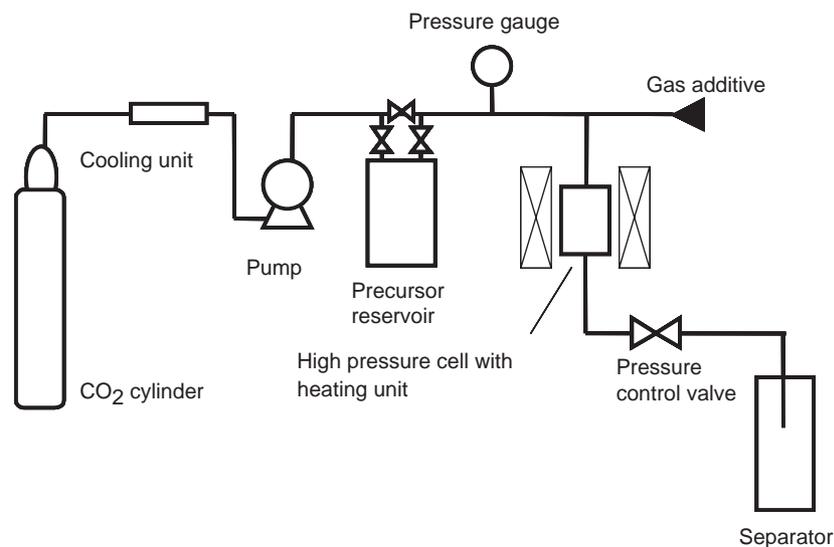


Fig. 1. Schematic diagram of the apparatus used in this work.

(discontinuous) using a gold sputter coater designed for the sample preparation for scanning electron microscopy. The film thickness was determined by a surface profilometer (DekTak™). The surfaces and cross-section of the deposited films were observed with JEOL JSM6500 field-emission scanning electron microscope (SEM) at an acceleration voltage of 20 kV. In order to characterize the crystal structure, or texture,  $\theta-2\theta$  X-ray diffraction was performed with Rigaku RAD1 X-ray diffractometer using Cu-K $\alpha$  emission line. The elemental composition and chemical status were analyzed with X-ray photoelectron spectroscopy (XPS) using Shimadzu ESCA750S or JEOL JPS9200. A pass energy of 100 eV and a spot size of approximately 1 mm square was used for the spectra recording. Sputtering was realized with 1 keV Ar<sup>+</sup> ion beam over 2 × 2 mm<sup>2</sup> area. No ion current was measured during this study. For depth analysis, Cu2p, C1s, O1s, and F1s photoemission lines were recorded after each sputtering step. The quantification of the film composition was made according to a standard procedure using the XPS apparatus database.

### 3. Results and discussion

#### 3.1. Basic deposition characteristics

It is well known that Cu(hfac)<sub>2</sub> well dissolves in common organic solvents such as alcohol [11]. Cu(hfac)<sub>2</sub> was very soluble in lower alcohols and ketones, as reported by Borgharkar et al. [11], but not in non-polar solvents such as n-hexane. ScCO<sub>2</sub> behaves like a gentle solvent and a reported value of the solubility of Cu(hfac)<sub>2</sub> in scCO<sub>2</sub> is 3.21 × 10<sup>-3</sup> mol/gCO<sub>2</sub> at 13.79 MPa and 40 °C [12]. In a preliminary experiment using a high pressure cell having view ports, Cu(hfac)<sub>2</sub> was confirmed to well dissolve in scCO<sub>2</sub> at 13 MPa and 30–80 °C and still very soluble at higher temperatures. This is in good agreement with an observation reported by M'Hamdi et al. [13] The solubility of Cu(hfac)<sub>2</sub> at higher temperatures have not been quantitatively documented. However, there is no doubt that the Cu(hfac)<sub>2</sub> dissolves in scCO<sub>2</sub> at elevated temperatures, because the vapor pressure Cu(hfac)<sub>2</sub> has a large positive temperature dependence.

Reaction deposits were observed at furnace temperatures above around 250 °C when the reactor was heated with the convection furnace (in the static arrangement). The temperature dependence of deposition is described later. The deposits obtained without H<sub>2</sub> were reddish-brown and rather granular. XRD and XPS showed the presence of crystalline Cu (see below). A significant improvement of the film quality was nevertheless observed when H<sub>2</sub> was added. The quality improvement stated here involves the appearance of a shiny copper color, the formation of a continuous film structure, an increase in deposition yield, and good experimental reproducibility. The yield of Cu was excel-

lently high, reaching almost 100 % under certain experimental conditions.

A preferential growth on conductive substances, including refractory metals, e.g. Fe, Au, Cu, WN, TiN, TaN and HF-treated p-Si, was observed. Shiny and continuous films were obtained on the metals, whereas a less shiny and continuous feature when deposited on the p-Si that received a laboratory-grade HF-treatment (Table 1). This tendency is known to occur also in CVD using Cu(hfac)<sub>2</sub> [14].

It should be noted that thin film formation is a heterogeneous process proceeding continuously at the substrate and growing film surfaces. Our observation on the surface dependence clearly indicates that the presence of conductive or metallic substances plays a key role in the most early nucleation. The addition of a reaction reagent, H<sub>2</sub> in our case, is also found to be important to initiate the heterogeneous reaction. Similar surface dependence has been observed in metal CVD [14–16], which suggests that a common growth mechanism is working.

#### 3.2. Film properties

Fig. 2 shows XPS (ex situ) surface survey spectra of the deposited Cu films. The as-deposited surfaces show carbon, oxygen, and fluorine impurities (a, c). Spectra b and d were taken after Ar etching for 60 s. The film deposited with H<sub>2</sub> (d) exhibits practically no trace of impurity elements, whereas, without H<sub>2</sub>, the impurities still reside in the films (b). XPS depth profiling was further performed for a film deposited with H<sub>2</sub>. The result shown in Fig. 3 also shows low level impurities in the film. Fig. 4 is  $\theta-2\theta$  XRD spectra of deposited Cu films. The (111) peak at 43 °C was predominant when H<sub>2</sub> was added, the preferential growth of which is known to be crucial to fabricating reliable ULSI interconnects. In contrast, the film obtained without H<sub>2</sub> showed a powder pattern, indicating random or even granular nature of the deposit. It is now very obvious that H<sub>2</sub> promotes the conversion of Cu(hfac)<sub>2</sub> to Cu. Hereinafter,

Table 1  
Summary of deposition runs

Medium	Substrate	Deposit	Color	Thickness
CO <sub>2</sub> +H <sub>2</sub>	HF-Si	Partially discontinuous	Reddish copper	T
	Si as-received	None	–	–
	Au-coated Si	Continuous	Shiny copper	VT
	TiN, TaN	Continuous	Shiny copper	T
	WN	Partially discontinuous	Bright copper	T
CO <sub>2</sub>	Fe, Cu	Continuous	Shiny copper	VT
	HF-Si	Granular	Reddish-brown	VT
Ar+H <sub>2</sub>	Au-coated Si	Granular	Reddish copper	VT
Ar	Au-coated Si	Tar-like	Dark brown	VT

VT: very thick; T: thick. Deposition conditions: 13 MPa, 350 °C (furnace), 15 min.

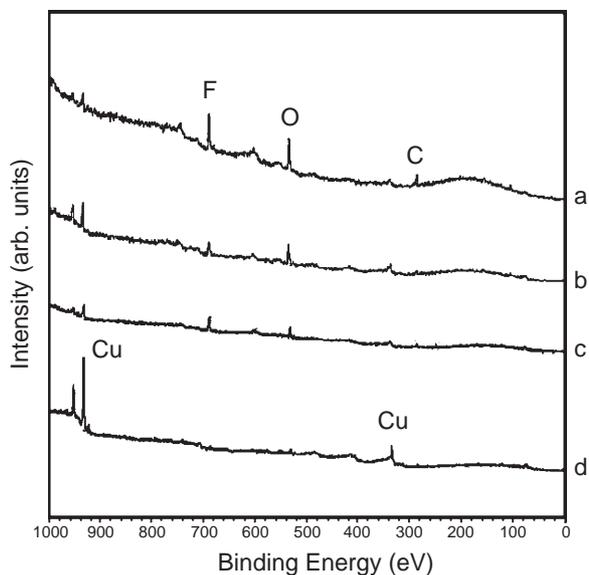


Fig. 2. X-ray photoelectron surface spectra of obtained films. (a) Without H<sub>2</sub>, as-deposited; (b) without H<sub>2</sub>, after ion etching; (c) with H<sub>2</sub>, as-deposited; (d) with H<sub>2</sub>, after ion etching.

only the deposition data obtained with H<sub>2</sub> will be discussed, unless otherwise specified.

The solid line in Fig. 5 is a reflectance spectrum taken from a 200 nm-thick Cu film deposited from scCO<sub>2</sub>. The reflectance was 90–95% of a sputtered Cu film (dotted line) in this wavelength range. Setting aside such a slight difference in the intensity, a more important feature is that the two profiles are almost identical. This obviously indicates the both films have a similar appearance. The resistivity of a 300 nm-thick as-deposited film on a sputtered TaN substrate was 2.15 μΩ cm.

Fig. 6 shows cross-sectional electron micrographs taken after a trial Cu filling into 250 nm (a) and 50 nm (b) narrow features, either measured at the bottom with SEM. Still apart from the optimization, good filling capability in HAR features is clearly demonstrated.

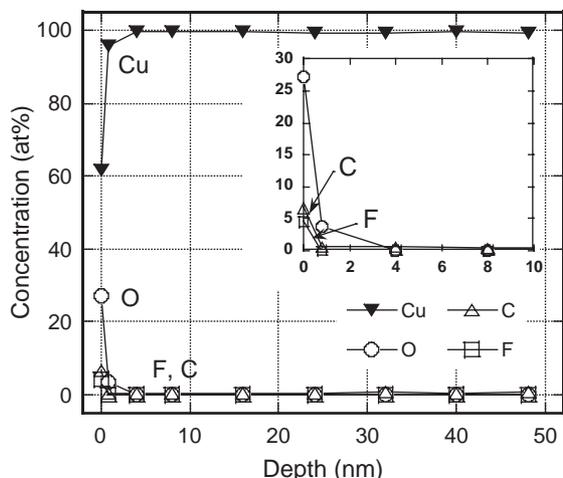


Fig. 3. XPS depth profiling of a deposited Cu film from scCO<sub>2</sub>. The inset magnifies the scales to show the surface impurities.

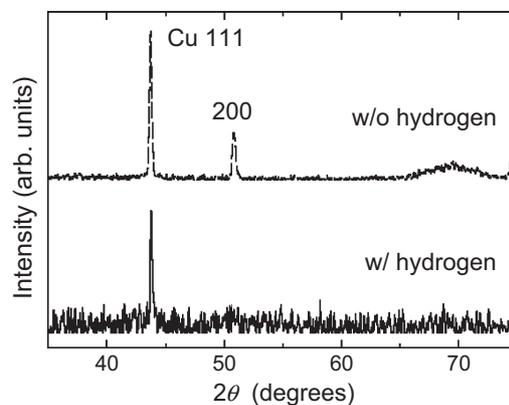


Fig. 4. θ–2θ X-ray diffraction scans of the films obtained without H<sub>2</sub> (above) and with H<sub>2</sub> (below).

### 3.3. Temperature dependence

#### 3.3.1. Static reactor

Fig. 7 shows a typical time-thickening profile obtained using the static reactor arrangement. The deposition was started by introducing the reactor in the isothermal region of the convection furnace maintained at 350 °C. An almost linear increase against elapsed time is observed. A nominal deposition rate calculated from this slope was 37 nm/min. Experimental values for different runs fall in the range of 30 to 50 nm/min. There was observed an incubation period of 5–7 min. The elapsed time in Fig. 7 was in fact recorded upon loading the reactor in the furnace. The delay in temperature increase, or the temperature difference between the furnace and the reactor interior, was significant, so that the reactor temperature was not constant during deposition. The temperature inside the reactor was measured in another run using a thermocouple of which tip was located at the volumetric center of the reactor. The result is also plotted in Fig. 7. It is shown that the substrate temperature reached about 150–180 °C when the film thickening started and that

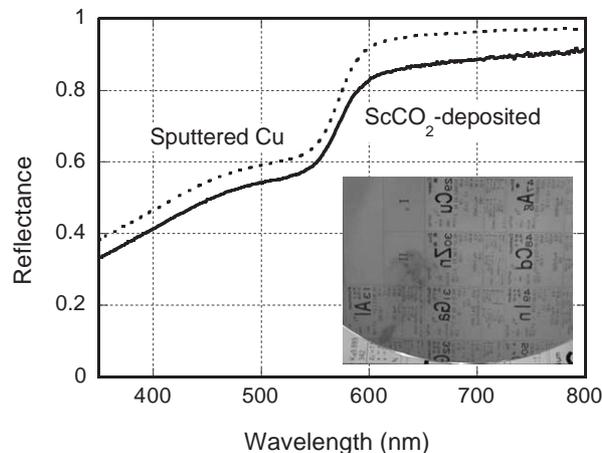


Fig. 5. Reflectance spectra of 200 nm-thick sputtered and scCO<sub>2</sub>-deposited Cu films. The inset shows the reflection of a periodical table on a Cu film deposited on a wafer.

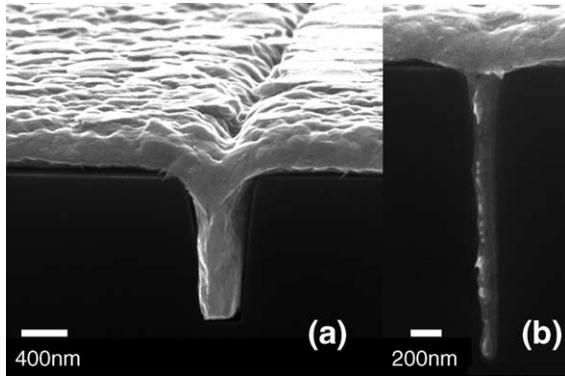


Fig. 6. SEM images of (a) 250 nm wide and (b) 50 nm wide trenches filled with Cu.

a significant duration was needed to reach the furnace temperature of 300 °C.

### 3.3.2. Semi-dynamic reactor

The temperature dependence of deposition was further investigated using the semi-dynamic arrangement, where a mixture of  $\text{scCO}_2$  and  $\text{Cu}(\text{hfac})_2$  was pumped into the closed-end reactor. The reactor temperature was maintained throughout at a constant temperature with a heating mantle, so that the delay in temperature increase was practically negligible. The reaction time was fixed at 15 min and atomic-layer-deposited (ALD) TiN wafer coupons were used as substrates.

Fig. 8 shows the appearance of the films obtained at different temperatures of 180–250 °C. The original surface, labeled TiN, was dark blue. Below 180 °C, there was practically no deposition seen. The surface turned metallic as the deposition temperature was increased. The film deposition rate were calculated by dividing the total film thickness by deposition time, and the logarithmic deposition rate was plotted against the reciprocal temperature (Fig. 9). The deposition rate showed a maxima at around 220 °C and then decreased with increasing temperature. The activation energy for deposition was evaluated at about  $0.42 \pm 0.12$  eV,

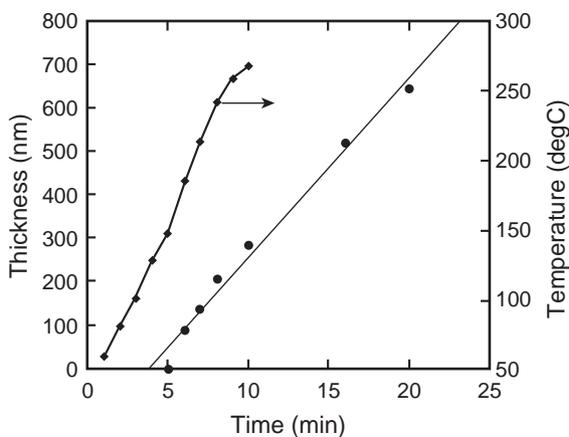


Fig. 7. Film thickness and reactor temperature plotted against deposition time using the static arrangement (see text).

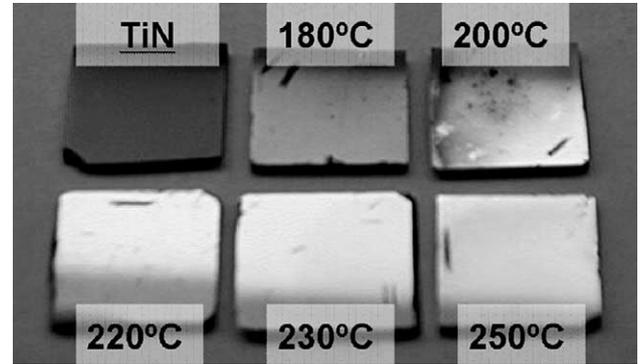


Fig. 8. Film surfaces deposited on TiN at various temperatures using a semi-dynamic arrangement.

where the data points from 180 to 230 °C were used ( $1000/T=1.99\text{--}2.21$ ). This value is almost one-half of the ones reported for CVD and is approximately same as for plasma-assisted CVD [17–19]. In addition, the deposition starting temperature, here of 180 °C, was about 100 °C lower than typical CVD temperatures obtained using  $\text{Cu}(\text{hfac})_2 + \text{H}_2$  chemistry[17].

Borgharkar et al. reported a low CVD starting temperature and a low activation energy when  $\text{Cu}(\text{hfac})_2$  was delivered as a solution in isopropanol [11]. Besides the similarity in using a solvent, the critical difference from the present work is lying. It is the role of the solvent indeed; in the latter isopropanol was vaporized in the deposition chamber and mainly served as the reduction agent for deposition. Contrarily,  $\text{CO}_2$  is chemically inert, at least it is not a strong proton donor even in the supercritical state. The role of  $\text{scCO}_2$  is discussed in the following section.

The decrease in thickness at higher temperatures is not a general observation in CVD. According to the CVD reaction chemistry, the deposition rate levels off at higher temperatures when the rate-determining step changes from the reaction-limited to the transport-limited of reaction

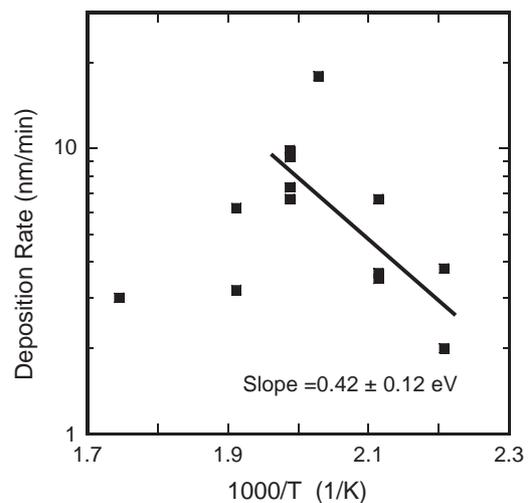


Fig. 9. Arrhenius plot of deposition rate obtained using the semi-dynamic arrangement. The slope (activation energy) was evaluated using the data for  $1000/T=1.99\text{--}2.21$  ( $T=180\text{--}230$  °C).

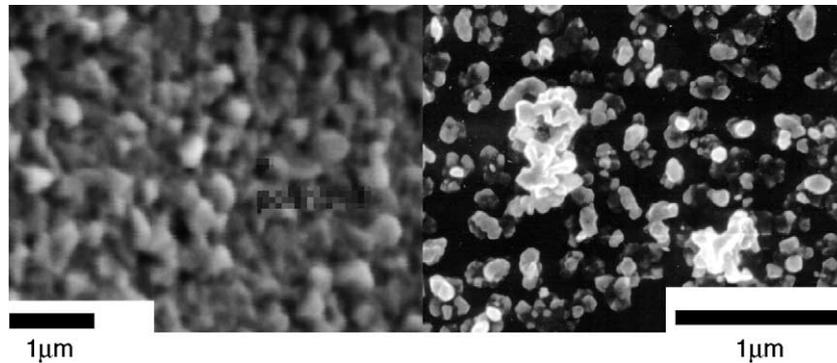


Fig. 10. SEM images of Cu films deposited using  $\text{scCO}_2$  (left) and  $\text{scAr}$  (right).

species, as have been often observed [18,19]. The transition temperatures reported in the literature were around 350 °C, which is much higher than our observation.

The deposition rate lowering at elevated temperatures is usually attributed to the presence of a reverse reaction or etching reaction. It is well known that Cu oxide can be etched by hexafluoroacetylacetone ( $\text{C}_5\text{H}_2\text{F}_6\text{O}_2$ ), denoted as Hhfac hereafter [20]. In our reaction system, Hhfac is a byproduct of Cu deposition reaction,  $\text{Cu}(\text{hfac})_2 + \text{H}_2 \rightarrow \text{Cu} + 2\text{Hhfac}$ : Our reaction system was a closed system, so that Hhfac will accumulate as the reaction proceeds. If the Cu oxidation reaction takes place simultaneously, the etching of Cu oxide may also proceed. However, such concurrent oxidation reaction under reductive chemistry is not very likely, judging from the good metallic nature of the deposited films. One possible cause for oxidation is the decomposition of  $\text{scCO}_2$ . This is known to take place under the presence of a certain catalyst. However, the decomposition temperature is generally higher than our deposition temperatures, thus this mechanism is still suppositional.

Another possible reason that account for the peaking of the deposition rate is the compressibility of  $\text{scCO}_2$ . The density of  $\text{scCO}_2$  varies with temperature, for instance, from  $3.36 \times 10^{-3}$  (230 °C,  $1000/T=1.99$ ) to  $2.54 \times 10^{-3}$  mol/ $\text{cm}^3$  (350 °C,  $1000/T=1.61$ ) at 13 MPa. Even if the pressure of  $\text{scCO}_2$  and the molar ratio of  $\text{Cu}(\text{hfac})_2$  are the same, the molecular number density decreases by 25% when the temperature is increased. However, the observed decrease in the deposition rate was much larger. It is noted that we have observed the same lowering of the deposition rate at higher temperatures when Cu was deposited from  $\text{scCO}_2$  using also  $\text{H}_2$  reduction chemistry [21]. We speculate this is a common phenomenon in the thin film growth from  $\text{scCO}_2$  at least for our system. However, detailed discussion is left for the further study.

#### 3.4. Critical role of $\text{scCO}_2$

As described so far, the supercritical fluid chemical deposition method satisfies basic requirements for depositing Cu thin films for ULSI interconnect application, such as

low resistivity, high reflectance, (111)-texturing, and deep gap-filling capability.

One reason that can account for the good filling capability and surface smoothness is the effect of high pressure. Impressively speaking, such a high pressure of the deposition environment seems to help force the dissolved precursor—and even deposited Cu—deep into the narrow features. Besides our intuition, the high total pressure, i.e., the high partial pressure of  $\text{Cu}(\text{hfac})_2$ , is not unreasonable to expect the good deposition topography. In the present case, the partial pressure of  $\text{Cu}(\text{hfac})_2$  was approximately 500 kPa, almost 3–4 orders of magnitude larger than that in usual CVD. There is a widely accepted belief that the nucleation density increases with the source material concentration. The high nucleation density promotes lateral film growth rather than forming isolated islands, which leads to smooth and conformable surface topography.

If the above assumption is the case, similar results are expected to occur also when using an inert gas such as Ar instead of  $\text{CO}_2$ . The critical point of Ar is 4.86 MPa and

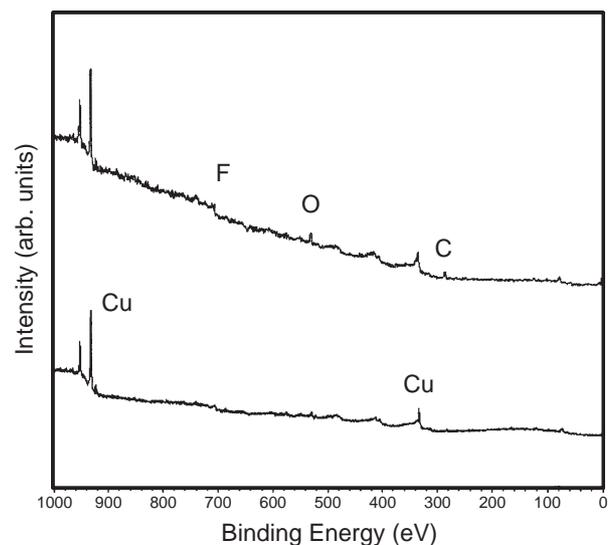


Fig. 11. X-ray photoelectron spectra of Cu films deposited using  $\text{scAr}$  (above) and  $\text{scCO}_2$  (below). After ion-etched for 60 s before acquisition.

150.7 K [22]; thus, under the same experimental conditions, Ar is also in the supercritical state.

We carried out the deposition using a mixture of supercritical Ar (scAr) and H<sub>2</sub>, fixing other deposition parameters. The deposit was obtained indeed on the substrate, however, was red-grown and very weakly adhered to the substrate. Fig. 10 right shows the surface topography of the deposit. We can see granular and very rough topography, compared to the one obtained using scCO<sub>2</sub> (Fig. 10, left). Fig. 11 compares XPS spectra of the films deposited using scAr+H<sub>2</sub> (above) and scCO<sub>2</sub>+H<sub>2</sub> (below) after ion etching for 60 s. The impurity elements were obviously observed when scAr was used.

A primary difference between scCO<sub>2</sub> and scAr is the presence of solvent capability. The larger solubility in the solvent, the larger interaction between the solvent and solute molecules. Hhfac is known to be more soluble in scCO<sub>2</sub> than its chelates [23]. The formation of a more soluble byproduct eases the overall deposition reaction, Cu(hfac)<sub>2</sub>+H<sub>2</sub>→Cu+2Hhfac, to proceed to the right-hand side. This leads to the suppression of impurities in the film and to an decrease in deposition temperature.

In addition, it is presumed that the solvent capability increases the mass transportation of either the leaving reaction byproducts or the incoming precursor. The former effect is crucial, otherwise the byproducts will reside at/near the growing surface causing the film deterioration. ScCO<sub>2</sub> deposition is thus a potentially clean and high-quality process compared to CVD.

#### 4. Conclusions

Cu thin film deposition through H<sub>2</sub> reduction of Cu(hfac)<sub>2</sub> was carried out using scCO<sub>2</sub> as a reaction solvent. The lowest deposition temperature was 180 °C which was about 100 °C lower than typical CVD starting temperatures. The (111)-preferential growth, high reflectance, and a low film resistivity of 2.15 μΩ cm were obtained. Remarkable filling capability to deep and narrow nano features was demonstrated.

The temperature dependence of the growth rate was studied, and the activation energy was determined at 0.42±0.12 eV. This value was lower than the ones of thermal CVD using the Cu(hfac)<sub>2</sub>-H<sub>2</sub> chemistry. Using scAr instead of scCO<sub>2</sub> resulted in the formation of a poor and granular film. The reason for these phenomena was discussed in terms of the solvent capability of scCO<sub>2</sub>.

This technique eases the use of solid precursors, and thus expands the capability of choosing stable precursors and of tailoring deposition chemistry. In addition it is potentially closed-loop and environmentally friendly, easy in reusing unreacted precursors, and compatible with supercritical cleaning. In conclusion, Cu deposition from supercritical fluids is a promising and versatile technology as a replace-

ment of conventional deposition techniques for ULSI metallization.

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