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Characteristics of copper deposition in a supercritical CO₂ fluid

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Abstract

Copper films were deposited in supercritical carbon dioxide through hydrogen reduction of Cu(hfac)₂ at pressures of 10–15 MPa and temperatures of 250–400 °C. Preferential deposition on conductive substrates was observed. X-ray photoelectron spectra of the films showed pronounced metallic Cu peaks and trace level of impurity elements. It was also found that the films were (111)-oriented. Copper filling into sub-half-micron high aspect ratio features was demonstrated.

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1. Introduction

Supercritical fluids (SCFs) have been so far successfully utilized in chemical processing and are now of considerable interest in applying to micro-fabrication. Advantageous characteristics of the SCFs in view of microprocessing are, for instance: (1) a wide controllability of molecular number density as functions of operating temperature and pressure, (2) high diffusivity and low viscosity allowing the penetration deep into small features, (3) solvent capability, and (4) ease in designing an environmentally friendly closed-loop system.

Metal deposition in SCFs from metalorganic precursors—so-called supercritical fluid chemical deposition (SFCD)—have been reported [1,2]. Recently, it was demonstrated that the SFCD technique is capable of filling metals into deci-nanometer small features [3]. We have independently started the study of Cu deposition in a supercritical CO₂ (denoted SC-CO₂) fluid, stimulated by the progress of SCFs in ultralarge-scale integrated circuit (ULSI) manufacturing [4–7], as a natural extension of the author's (EK) work in chemical vapor deposition (CVD) for ULSI metallization [8].

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This paper reports on Cu deposition characteristics from hexafluoroacetylacetonate-copper ($\text{Cu}(\text{hfac})_2$) in a supercritical CO_2 fluid. $\text{Cu}(\text{hfac})_2$ is one of common Cu precursors for Cu CVD [9–11], and has also been used in SFCD [2]. The $\text{Cu}(\text{hfac})_2$ is known to well dissolve in common organic solvents such as alcohol [10]. This solubleness meets the requirement for deposition in a non-gaseous fluid as a reaction medium. It is noted such common solvents are often used in SC- CO_2 as an entainer.

2. Experimental

Carbon dioxide, hydrogen, and $\text{Cu}(\text{hfac})_2$ were introduced into a high-pressure reaction cell. The liquid CO_2 was pumped using a plunger pump of a liquid chromatograph to attain a pressure above the critical point of CO_2 (7.38 MPa, 31 °C). The concept of this experimental setup is similar to the apparatus reported in literature [2]. The pressures and temperatures were 10–15 MPa and 250–400 °C, respectively. The $\text{Cu}(\text{hfac})_2$ was purchased from TRI Chemical Lab., Inc. (Yamanashi, Japan). The $\text{Cu}(\text{hfac})_2$ was handled in a N_2 -filled glove box to avoid hydration. A typical molar ratio of H_2 to $\text{Cu}(\text{hfac})_2$ was about 10.

Silicon(100) wafer pieces were mainly used in deposition experiments. The wafer pieces received precleaning by using a 2% HF solution, diluted with laboratory DI water, and/or coating with Au by using a sputtering tool for electron micrography. Trench/contact-hole test-pattern substrates having a WN layer on top were also used to demonstrate filling capability.

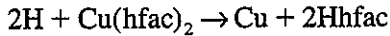
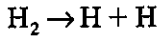
The deposits were characterized with secondary electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

SC- CO_2 is known to behave like a gentle solvent. $\text{Cu}(\text{hfac})_2$ was very soluble in lower alcohols and ketones but showed a poor solubility in hexane at room temperature. In supercritical CO_2 near room temperature, $\text{Cu}(\text{hfac})_2$ seemed to have a larger solubility than hexane. It was reported that Cu β -diketonate complexes dissolve well in SC- CO_2 [1]. We observed a good dispersion of $\text{Cu}(\text{hfac})_2$ to occur in SC- CO_2 at elevated temperatures.

The deposits obtained without H_2 were reddish-brown and rather granular. XRD and XPS showed the presence of crystalline Cu (see below). A significant improvement of the film quality is nevertheless observed when H_2 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. The Cu films deposited preferentially on metallic substrates such as Au-coated wafers and HF-treated Si. On insulating surfaces, the deposited films showed a similar appearance in the case of no H_2 addition.

Such effects of H_2 are similar to chemical vapor deposition [11]. This similarity suggests that the surface dissociation of H_2 is involved in the deposition mechanism as the rate-determining step. A possible reaction scheme is, for instance:



Adsorption of CO_2 and formation of other byproducts such as formic acid may compete.

The deposition rates obtained were 30–50 nm/min. These values are comparable to the ones reported in CVD [10,11] and is practically sufficient at sub-100 nm technology nodes. The yield of Cu was excellently high, reaching almost 100% under certain experimental conditions. This high yield makes SFCD very attractive against Cu CVD; in the latter most of the Cu source is exhausted and wasted.

Fig. 1 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 are taken after Ar etching at 2 keV for 60 s. The film deposited with H_2 (spectrum d) exhibits practically no trace of impurity elements; however, without H_2 , the impurities still reside in the films. It is obvious that H_2 promotes the conversion of $\text{Cu}(\text{hfac})_2$ to Cu.

Fig. 2 is an XRD spectrum of a Cu film deposited on a Au-coated Si wafer using H_2 . The (111) peak at 43° is predominant, indicating the preferential growth of (111) faces parallel to the surface.

Copper was filled into sub-halfmicron features engraved in 2- μm thick silicon dioxide. Fig. 3 shows a cross-sectional electron micrograph taken after Cu filling. It is seen that Cu is conformally deposited in 0.45 μm features. Small voids are however observed near bottom; this is speculated to be due to poor coverage of Au coated with a common sputtering tool for electron micrography, therefore, not to be due to the limitation of SFCD.

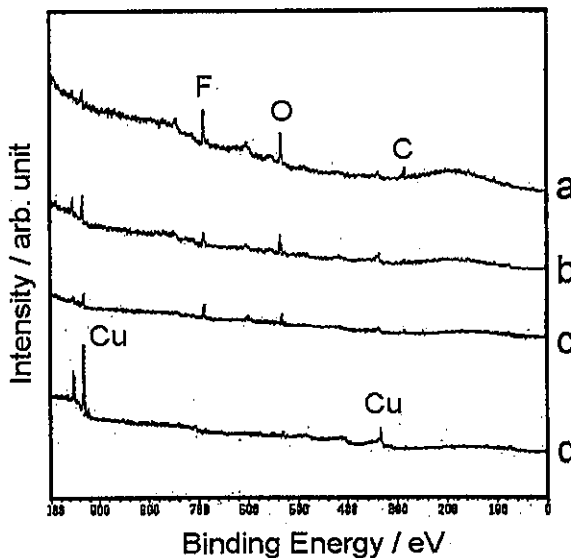


Fig. 1. XPS surface survey spectra of Cu films. (a) no H_2 , before Ar etch; (b) no H_2 , etched 60 s; (c) with H_2 , before Ar etch; (d) with H_2 , etched 60 s.

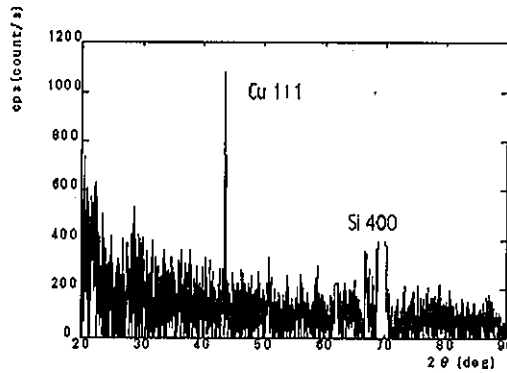


Fig. 2. XRD spectrum of a Cu film deposited on Au-coated Si wafer using H_2 .

4. Conclusions

Cu was deposited in supercritical CO_2 from $Cu(hfac)_2$. $Cu(hfac)_2$ was found to disperse in the SC- CO_2 very well at elevated temperatures. Good quality films—having a metallic appearance and very low impurities—were deposited when H_2 was added as reductant. A preferential growth was observed on metallic surfaces. This indicates that hydrogen dissociation is involved in the growth mechanism, probably as the rate-determining step, as reported for chemical vapor deposition [12]. The films were (111)-oriented, which satisfies one of fundamental requirements for ULSI application. A good filling capability in submicron features was also demonstrated. In conclusion, the supercritical fluid chemical deposition is of a potential replacement of chemical vapor and electro/electroless deposition being currently used in ULSI manufacturing.

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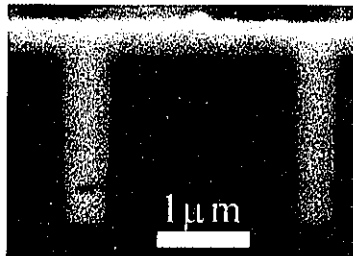


Fig. 3. SEM photo of $0.4 \mu m$ holes after supercritical filling.

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