

# Kinetics of Sublimation of Copper(II) Acetylacetonate Complex Used for Chemical Vapor Deposition of Copper Films

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Received February 22, 1990. Revised Manuscript Received September 26, 1990

The kinetics of sublimation of copper(II) acetylacetonate complex,  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ , in pure hydrogen or argon was investigated by isothermal thermogravimetry at a temperature and pressure ranging from 140 to 210 °C and 100 to 300 Torr, respectively. The sublimation rate of this compound was independent of time and was observed to be inversely proportional to the  $\text{H}_2$  or Ar pressure. The apparent activation energy of the sublimation process was equal to  $105.3 \pm 9$  kcal mol<sup>-1</sup>. The diffusion of copper complex vapor in the  $\text{H}_2$  or Ar gas phase from the boat to the cold wall of the reactor may be the rate-limiting step of the sublimation process. Chemical vapor deposition of pure copper films was performed for the first time by decomposition of this copper complex at low temperatures (220–250 °C) in  $\text{H}_2$  or  $\text{H}_2$ -Ar carrier gas. The structure or morphology of copper films tightly adherent to  $\text{SiO}_2/\text{Si}$  substrates was found to depend on the deposition time, deposition temperature and composition of the gas phase used as a carrier gas.

## Introduction

Metal films produced by chemical vapor deposition (CVD) at low temperatures are of interest for numerous microelectronic applications, in particular for use in packaging metallization. Various metal halides and metal carbonyls are currently employed as gaseous precursors for CVD of metal coatings.<sup>1</sup> In general, these starting materials suffer from two major limitations for use in microelectronics: (i) the deposition of metal films by the  $\text{H}_2$  reduction of metal halides occurs at relatively high temperatures; (ii) the thermal decomposition of metal carbonyls provides oxygen- and carbon-contaminated films with significantly high resistivities.<sup>2</sup> Now, various metal precursors are being investigated to deposit pure metal films at low temperatures compatible with advanced microelectronic materials or structures.<sup>3-5</sup> Copper-containing thin films were chemically vapor deposited from copper halides or copper complexes listed in Table I. The de-

Table I. Chemical Vapor Deposition (CVD) of Copper-Containing Thin Films

exptl method	metal precursor or gas atm	deposited mater	ref
conventional CVD	$\text{CuF}_2$ or $\text{CuF}$	copper	6, 7
conventional CVD	$\text{CuCl}_2$ or $\text{CuCl}$	copper	8
conventional CVD	$\text{Cu}(\text{tfacac})_2$ or $\text{Cu}(\text{hfacac})_2\text{-H}_2\text{O-H}_2^a$	copper	9
conventional CVD	$\text{Cu}(\text{hfacac})_2\text{-Ar}^a$	copper	10
conventional CVD	copper(I) <i>tert</i> -butoxide	copper or $\text{Cu}_2\text{O}$	11
laser-assisted CVD	$\text{Cu}(\text{hfacac})_2^a$	copper	12-17
laser-assisted CVD	$\text{Cu}(\text{hfacac})_2(\text{ethanol})_x^b$	amorphous copper-carbon complex	15, 18
laser-assisted CVD	(triethylphosphine)-cyclopentadienyl-copper(I)	copper or copper oxide	19
plasma-enhanced CVD	$\text{Cu}(\text{hfacac})_2\text{-H}_2\text{O-H}_2\text{-Ar}^a$ or $\text{O}_2\text{-Ar}$	copper or copper oxide	20

<sup>a</sup>Tfacac = trifluoroacetylacetonate,  $\text{C}_5\text{F}_3\text{H}_4\text{O}_2$ ; hfacac = hexafluoroacetylacetonate,  $\text{C}_5\text{F}_6\text{H}_2\text{O}_2$ . <sup>b</sup>Mono ( $x = 1$ ) or bis ( $x = 2$ ) ethanolate complex.

position process from copper complexes was based on the decomposition of the vapor phase by conventional thermal activation, plasma activation or under laser irradiation. Appreciable fluoride contaminants can be expected in the layers when using fluorinated compounds as precursors.<sup>12,20</sup> Accordingly, copper bearing molecules free of halogen are of interest to produce pure copper films. The deposition of copper oxide based high-temperature superconductor films was achieved from copper(II) acetylacetonate complex,  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$  or  $\text{Cu}(\text{acac})_2$ ,<sup>21</sup> this solid compound sublimated at 140 °C in an argon carrier stream. The possibility to use this complex as a starting material for CVD of pure copper films was not yet explored. For this type of deposition process, the precursor needs to possess

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desirable properties including high sublimation rate, stability in the sublimation vessel, and low decomposition temperatures, which remain to be investigated in detail.

This paper deals with the results of experiments designed to study the kinetics of sublimation of  $\text{Cu}(\text{acac})_2$  as a function of various parameters such as argon or hydrogen pressure and temperature. In addition, the results of the preliminary study of the CVD of copper films are described; in particular the effects of the deposition temperature and composition of gas ambient on the structure or morphology of copper films are reported.

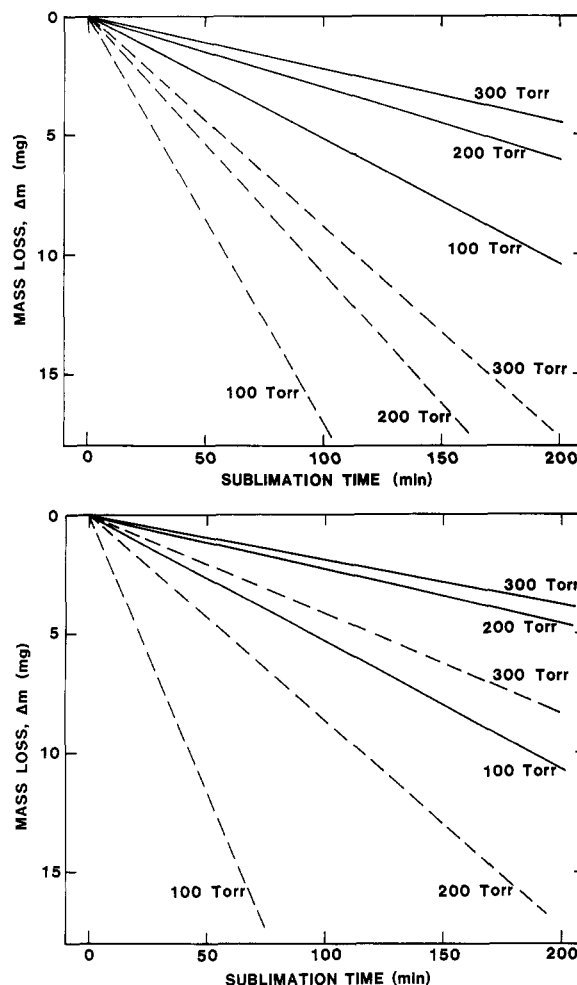
### Experimental Section

The kinetics of sublimation of  $\text{Cu}(\text{acac})_2$  was investigated by thermogravimetry using an Uguine-Eyraud system, Model B-70. The thermogravimetric analyzer was equipped with facilities for isothermal and vacuum or reduced pressure operations. The powdery copper complex with a purity of 97.7% was supplied by Lancaster Synthesis Ltd. The X-ray diffraction pattern of this material was compared to ASTM data; all diffraction peaks of the experimental X-ray pattern could be ascribed to  $\text{Cu}(\text{acac})_2$ . The mass loss of the boat containing 50–150 mg of  $\text{Cu}(\text{acac})_2$  was recorded as a function of time at a series of constant temperature and pressure. The sublimation temperature and hydrogen or argon pressure were fixed at values in the ranges 140–210 °C and 100–300 Torr, respectively. The first 10–30 min of the sublimation experiments was needed to stabilize the temperature of samples. The mass loss occurring for this stabilization step was eliminated from the kinetic measurements. The solid compound condensed during the sublimation experiments on the walls of the thermoanalyzer at room temperature was identified to be  $\text{Cu}(\text{acac})_2$  by X-ray diffraction technique.

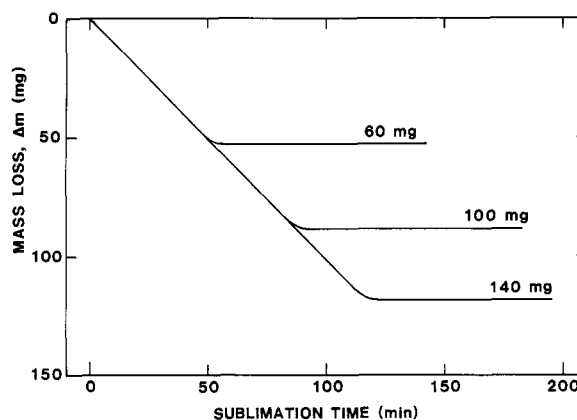
The deposition of copper films was performed in a horizontal Pyrex tube heated by a conventional resistance furnace. The boat containing 1–2 g of copper complex was placed in the CVD reactor at the inlet of the gas carrier stream. Thermal oxide coated monocrystalline silicon substrates ( $2 \times 2 \text{ cm}^2$ ) were maintained on a substrate holder at the center of the CVD furnace. The sublimation temperature of  $\text{Cu}(\text{acac})_2$  and the deposition temperature of films measured by thermocouples were varied from 180 to 200 and 225 to 250 °C, respectively. The films were grown by using hydrogen–argon (1:1) mixtures or pure hydrogen as a carrier gas. The total flow rate and total pressure were fixed at 3 L/min and 1 atm, respectively. The films deposited on  $\text{SiO}_2/\text{Si}$  substrates were characterized by X-ray diffraction techniques, Auger electron spectroscopy, and scanning electron microscopy.

### Results and Discussion

**Sublimation of  $\text{Cu}(\text{acac})_2$ .** The mass loss of the cylindrical boat ( $83 \text{ mm}^2$  in section area) filled with copper complex was recorded as a function of time at constant temperature and hydrogen or argon pressure. Typical thermogravimetric curves are given in Figure 1. The sublimation rate of  $\text{Cu}(\text{acac})_2$  remains constant for the sublimation times investigated. In addition, at a given temperature, the sublimation rate decreases with increasing  $\text{H}_2$  or Ar pressure and is higher in hydrogen than in argon atmosphere. Some experiments were continued until the mass of the boat reached a constant value. At temperatures lower than 190 °C, the boat was empty at the end of these experiments, showing that only the sublimation of  $\text{Cu}(\text{acac})_2$  occurred under these experimental conditions. A small amount of solid residue (less than 5% of the initial mass of  $\text{Cu}(\text{acac})_2$ ) was found in the boat after experiments at 200 °C in  $\text{H}_2$  or at 210 °C in Ar ambient. This residue identified by X-ray diffraction technique was copper or copper oxides for decomposition in hydrogen or argon atmosphere, respectively. As a result, the onset of the thermal decomposition of  $\text{Cu}(\text{acac})_2$  occurred between 190 and 210 °C depending upon the nature of the gas atmosphere. However, under these experimental conditions, the contribution of the sublimation process to the

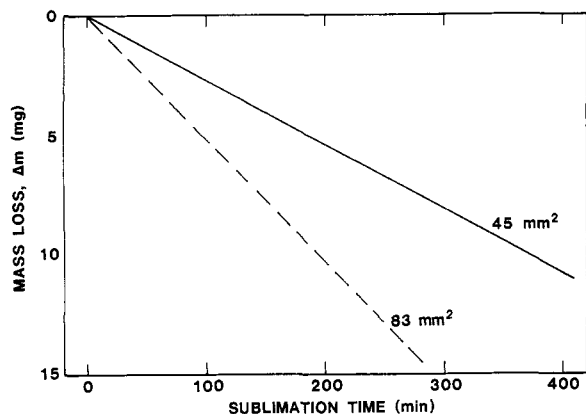


**Figure 1.** Thermogravimetric curves for sublimation of  $\text{Cu}(\text{acac})_2$ ; (top) under various pressures of hydrogen (1 Torr = 133 Pa) at 140 (solid lines) and 160 °C (dashed lines); (bottom) under various pressures of argon at 160 (solid lines) and 180 °C (dashed lines).

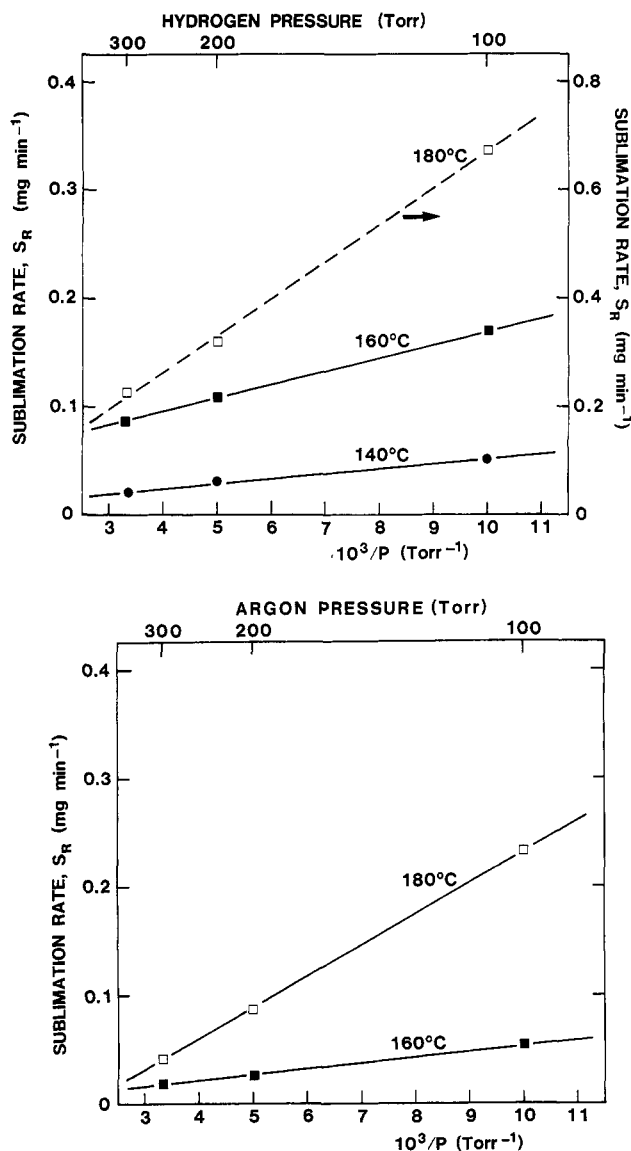


**Figure 2.** Effect of the initial mass of  $\text{Cu}(\text{acac})_2$  on the kinetics of sublimation at 210 °C under 100 Torr of argon.

total mass loss of samples was larger than 90%. At 210 °C in Ar ambient, the rate of the mass loss of the boat essentially equal to the sublimation rate of  $\text{Cu}(\text{acac})_2$  was found to be independent of the initial mass of copper complex (Figure 2). This result suggests that the kinetics of the sublimation process is independent of the specific surface area of the powdery compound. The grain size of  $\text{Cu}(\text{acac})_2$  was small enough to consider the samples as a closely packed powdery structure. The sublimation zone was limited to the surface area of the macroscopic gas–solid

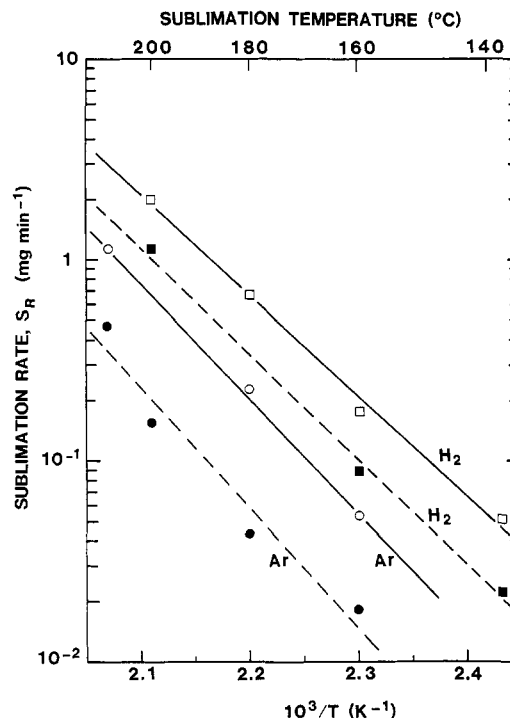


**Figure 3.** Effect of the section area of the cylindrical boat on the kinetics of sublimation of  $\text{Cu}(\text{acac})_2$  at  $160^\circ\text{C}$  under 100 Torr of argon.



**Figure 4.** Top: hydrogen pressure effect on the sublimation rate of  $\text{Cu}(\text{acac})_2$  at various sublimation temperatures. Bottom: argon pressure effect on the sublimation rate of  $\text{Cu}(\text{acac})_2$  at various sublimation temperatures.

interface, i.e., to the section area of the cylindrical boat. The effect of the section area of the boat on the mass loss was measured at  $160^\circ\text{C}$  with an Ar pressure of 100 Torr (Figure 3). The sublimation rate of  $\text{Cu}(\text{acac})_2$  was ob-



**Figure 5.** Arrhenius diagram for sublimation of  $\text{Cu}(\text{acac})_2$  under 100 (solid lines) or 300 Torr (dashed lines) of hydrogen or argon.

served to be proportional to the square of the boat diameter.

The  $\text{H}_2$  or Ar pressure effect on the sublimation rate of  $\text{Cu}(\text{acac})_2$  is exhibited in Figure 4. The accuracy on the sublimation rate was estimated to be about 5% on the basis of the reproducibility of the sublimation process and sensibility of the thermogravimetric analyzer. The sublimation rate is inversely proportional to the  $\text{H}_2$  or Ar pressure. The temperature effect on the sublimation rate in  $\text{H}_2$  or Ar ambient is shown in the Arrhenius diagram in Figure 5. The sublimation process complies with the Arrhenius law. Assuming an accuracy of 5% on the sublimation rate, the Arrhenius curves corresponding to various experimental conditions of sublimation can be considered essentially as parallel straight lines. The apparent activation energy of the sublimation process deduced from the slope of the straight lines can be considered to be independent of the pressure and nature of ambient gas; the average value is equal to  $(105 \pm 9) \text{ kJ mol}^{-1}$ .

Three main steps are involved in the sublimation process of  $\text{Cu}(\text{acac})_2$ : (1) desorption of  $\text{Cu}(\text{acac})_2$  molecules; (2) diffusion of these molecules in the  $\text{H}_2$  or Ar gas phase; (3) condensation of  $\text{Cu}(\text{acac})_2$  molecules on the cold wall of the tube at the outlet of the furnace.

The gas-phase diffusion step can be considered to occur in one direction only along the axis Ox which is the axis of the vertical cylindrical tube of the thermogravimetric analyzer, through an isothermal zone with a length  $L$  that is half furnace length (the boat was placed at the center of the vertical furnace).

The sublimation rate of  $\text{Cu}(\text{acac})_2$  can be expressed as follows:

$$S_R = -dn_1/dt \quad (1)$$

where  $dn_1$  is the number of  $\text{Cu}(\text{acac})_2$  molecules per  $\text{cm}^2$  leaving the gas-solid interface during the time  $dt$ .

Assuming that the gas-phase diffusion is the rate-limiting step, the desorption and condensation steps of  $\text{Cu}(\text{acac})_2$  are at equilibrium; therefore, considering ideal gas behavior, the vapor pressure of  $\text{Cu}(\text{acac})_2$  at the gas-solid

interface is equal to the saturation vapor pressure, i.e.

$$P_0 = \exp[-(\Delta H/RT) + (\Delta S/R)] \quad (2)$$

where  $R$  is the ideal gas constant and  $T$  is the sublimation temperature;  $\Delta H$  and  $\Delta S$  are the standard enthalpy and entropy of sublimation of  $\text{Cu}(\text{acac})_2$ , respectively.

From this assumption, the sublimation rate is equal to the flux of diffusion:

$$S_R = -dn_1/dt = -D_{1(12)} dC_1/dx \quad (3)$$

In this equation,  $D_{1(12)}$  is the diffusion coefficient of  $\text{Cu}(\text{acac})_2$  molecules in hydrogen or argon, i.e.

$$D_{1(12)} = v_1 \lambda_{1(12)}/2 \quad (4)$$

where  $v_1$  and  $\lambda_{1(12)}$  are the average velocity and the mean free path of molecules in  $\text{H}_2$  or argon, respectively;<sup>22</sup>  $dC_1/dx$  is the concentration gradient of  $\text{Cu}(\text{acac})_2$  molecules, which can be considered as a linear gradient between the boat and the cold wall; therefore

$$dC_1/dx = -C_0/L \quad (5)$$

where  $C_0$  is the concentration of  $\text{Cu}(\text{acac})_2$  molecules at the gas–solid interface; in addition, the concentration of  $\text{Cu}(\text{acac})_2$  in the gas phase over the cold wall is negligible with respect to  $C_0$ .

As a result, the sublimation rate can be expressed as follows:

$$S_R = -dn_1/dt = C_0 v_1 \lambda_{1(12)}/(2L) \quad (6)$$

Assuming a Maxwellian distribution of the average velocity, the average velocity and the mean free path of molecules are given by<sup>22</sup>

$$v_1 = (8RT/\pi M_1)^{1/2} \quad (7)$$

or

$$C_0 v_1 = 4N_A P_0 / (2\pi M_1 RT)^{1/2} \quad (8)$$

$$\lambda_{1(12)} = v_1 / (Z_1 + Z_{1(12)}) \quad (9)$$

where  $N_A$  is the Avogadro number,  $M_1$  the molar mass of  $\text{Cu}(\text{acac})_2$ ,  $P_0$  the saturation vapor pressure of  $\text{Cu}(\text{acac})_2$  at the sublimation temperature  $T$ ,  $Z_1$  the frequency at which a given  $\text{Cu}(\text{acac})_2$  molecule collides with others, and  $Z_{1(12)}$  the frequency at which a  $\text{Cu}(\text{acac})_2$  molecule collides with  $\text{H}_2$  or Ar molecules.

These collision frequencies are given by

$$Z_1 = 4(\sigma_1)^2(\pi RT/M_1)^{1/2}(N_A P_0/RT) \quad (10)$$

$$Z_{1(12)} = 2(2)^{1/2}(\sigma_{12})^2(\pi RT/\mu_{12})^{1/2}(N_A P_2/RT) \quad (11)$$

with

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \quad (12)$$

$$\mu_{12} = (M_1 M_2)/(M_1 + M_2) \quad (13)$$

In these expressions,  $\sigma_1$  and  $\sigma_2$  are the collision diameters of  $\text{Cu}(\text{acac})_2$  and  $\text{H}_2$  (or Ar) molecules, respectively, and  $M_2$  and  $P_2$  the molar mass and pressure of the buffer gas ( $\text{H}_2$  or Ar), respectively.

In our sublimation experiments, the hydrogen or argon pressure was considerably higher than the saturation vapor pressure of  $\text{Cu}(\text{acac})_2$ . Therefore, the total pressure  $P$  was approximately equal to the hydrogen or argon pressure; in addition, the total collision frequency,  $Z = (Z_1 + Z_{1(12)})$ , was equal to  $Z_{1(12)}$ .

Considering that  $P = P_2$  and  $P \gg P_0$ , the mean free path of  $\text{Cu}(\text{acac})_2$  molecules is given by

$$\lambda_{1(12)} = \{1/[\pi(\sigma_{12})^2 N_A]\}[M_2/(M_1 + M_2)]^{1/2}(RT/P) \quad (14)$$

Substituting  $(C_0 v_1)$  and  $\lambda_{1(12)}$  (given by eqs 8 and 9–13, respectively), eq 6 becomes

$$S_R = -dn_1/dt = k(RT)^{1/2}(P_0/P) \quad (15)$$

with

$$k = (2)^{1/2}\{1/[L(\pi)^{3/2}(\sigma_{12})^2(M_1)^{1/2}]\}[M_2/(M_1 + M_2)]^{1/2} \quad (16)$$

The mass loss,  $dm$ , of the sample during the time  $dt$  is proportional to  $dn_1$ ; therefore, the integration of eq 14 leads to

$$\Delta m = (k'/P)(RT)^{1/2} \exp[-(\Delta H/RT) + (\Delta S/R)]t \quad (17)$$

or

$$\Delta m = Kt \quad (18)$$

where  $\Delta m$  is the mass loss of the sample per  $\text{cm}^2$  of the sublimation area.

Equation 18 shows that the mass loss of samples varies linearly with time at a constant temperature and pressure; this dependence was observed experimentally. Furthermore, the calculated sublimation rate,  $d(\Delta m)/dt = K$ , derived from this sublimation mechanism is given by

$$K = (k'/P)(RT)^{1/2} \exp[-(\Delta H/RT) + (\Delta S/R)] \quad (19)$$

i.e., at a constant temperature, the calculated sublimation rate is inversely proportional to the total pressure,  $P$ . This sublimation rate dependence on  $\text{H}_2$  or Ar pressure was also observed in our sublimation experiments.

At a constant  $\text{H}_2$  or Ar pressure, the calculated sublimation rate depends on the sublimation temperature as follows:

$$\log K = -(\Delta H/2.3RT) + (1/2) \log T + \text{constant} \quad (20)$$

In a narrow temperature range (for example, 140–210 °C), the variation of  $\log T$  can be neglected with respect to the variation of  $(\Delta H/2.3RT)$ . Therefore, the curve  $\log K = f(1/T)$  is linear and

$$\log K = -(\Delta H/2.3RT) + C' = -(E/2.3RT) + C' \quad (21)$$

The Arrhenius diagram (Figure 5) shows that the experimental sublimation rate can be expressed as a function of the sublimation temperature by an equation similar to eq 21.

In addition, the apparent activation energy deduced from the Arrhenius diagram would be equal to the standard enthalpy of sublimation of  $\text{Cu}(\text{acac})_2$ . The values of this sublimation enthalpy given in the literature as well as the experimental conditions of measurements are reported in Table II. The value of 105.6  $\text{kJ mol}^{-1}$  deduced from our experimental study is in good agreement with three values obtained from vapor pressure–temperature measurements,<sup>26</sup> by thermogravimetry in a lower temperature range,<sup>27</sup> or by differential scanning calorimetry.<sup>30</sup>

In fact, the experimental values of the standard enthalpy of sublimation of copper(II) acetylacetonate complex given in the literature can be classified into two groups, namely,  $\Delta H^\circ = 50.6\text{--}57.3 \text{ kJ mol}^{-1}$  and  $\Delta H^\circ = 106.1\text{--}109.5 \text{ kJ mol}^{-1}$  (Table II). This large deviation by a factor of 2 may originate from a dimerization of the copper complex. Indeed,

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Table II. Standard Enthalpy of Sublimation of Copper(II) Acetylacetonate Complex,  $\text{Cu}(\text{acac})_2$ 

compd	$\Delta H$ , $\text{kJ mol}^{-1}$	temp, $^{\circ}\text{C}$	exptl method	year	ref
$\text{Cu}(\text{tfacac})_2^a$	50.6			1960	23
$\text{Cu}(\text{tfacac})_2^a$	50.6	100–150	vapor pressure–temp measts	1965	24
$\text{Cu}(\text{acac})_2$	62.8		est from data reported in ref 23	1962	25
$\text{Cu}(\text{acac})_2$	109.5	95–160	vapor pressure–temp measts	1970	26
$\text{Cu}(\text{acac})_2$	106.1	60–90	thermogravimetry	1971	27
$\text{Cu}(\text{acac})_2$	57.3	200–280	differential scanning calorimetry	1971	28
$\text{Cu}(\text{acac})_2$	57.1	40–170	torsion effusion method	1981	29
$\text{Cu}(\text{acac})_2$	$107.1 \pm 5.7$	170–225	differential scanning calorimetry	1987	30
$\text{Cu}(\text{acac})_2$	$105.3 \pm 9$	140–210	thermogravimetry	this work	

<sup>a</sup>Tfacac = trifluoroacetylacetonate,  $\text{C}_5\text{F}_3\text{H}_4\text{O}_2$ .

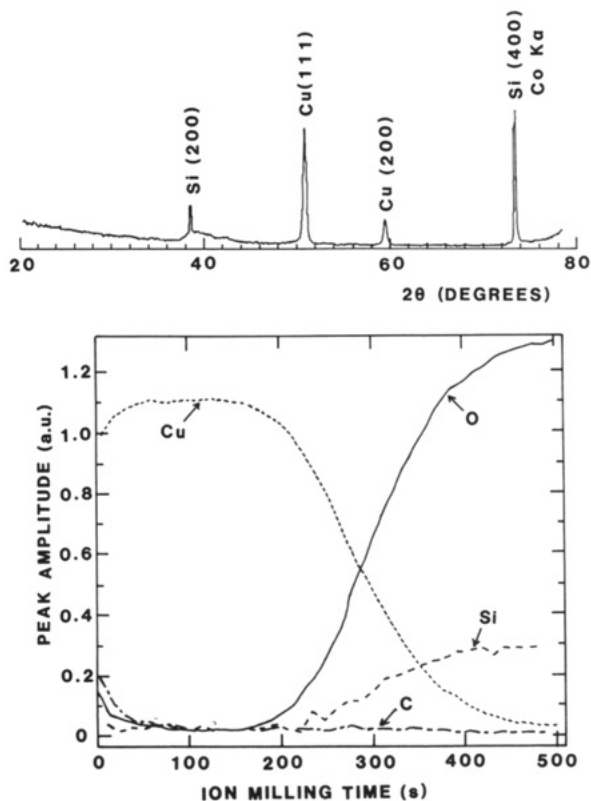


Figure 6. Top: typical X-ray diffraction pattern of  $\text{Cu}/\text{SiO}_2/\text{Si}$  structures. Auger depth profiles of elements in  $\text{Cu}/\text{SiO}_2/\text{Si}$  structures provided by measuring the peak amplitude of the following Auger transitions: Cu (LMM, 920 eV), O (KLL, 510 eV), Si (KLL, 92 eV), and C (KLL, 272 eV). The copper peak amplitude was multiplied by a factor of 0.5.

dimer or oligomer compounds can be found for this type of metal complexes.<sup>5,31</sup> However, this discrepancy also can result from various other sources of error in the experimental procedures or methods used for measurements of thermodynamic data, e.g., the temperature range investigated by Beech and Lintonbon<sup>28</sup> encompassed the decomposition temperature (about 210  $^{\circ}\text{C}$ ) of the copper complex.

**Chemical Vapor Deposition of Copper Films.** Thin films were deposited on oxidized monocrystalline silicon substrates by decomposition of  $\text{Cu}(\text{acac})_2$  vapor in pure hydrogen or  $\text{H}_2$ -Ar (1:1) gas mixtures at atmospheric pressure between 225 and 250  $^{\circ}\text{C}$  for 10–30 min. The material deposited under these conditions was tightly adherent to  $\text{SiO}_2$ . The structure of these films was investigated by X-ray diffraction techniques using a Co anticathode as an X-ray source. The X-ray diffraction patterns of these films exhibited sharp diffraction peaks

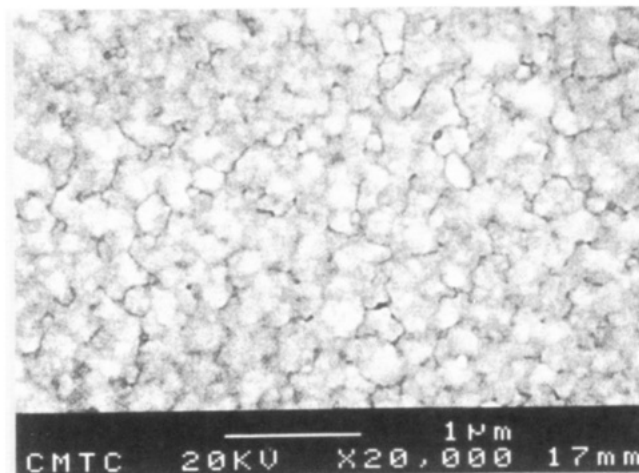


Figure 7. Surface morphology of copper films deposited at 250  $^{\circ}\text{C}$  for 10 min in an  $\text{H}_2$ -Ar (1:1) gas flow.

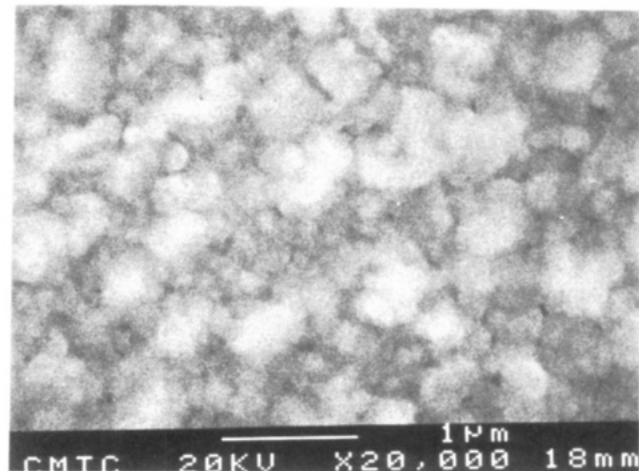


Figure 8. Surface morphology of copper films deposited at 250  $^{\circ}\text{C}$  for 20 min in an  $\text{H}_2$ -Ar (1:1) gas flow.

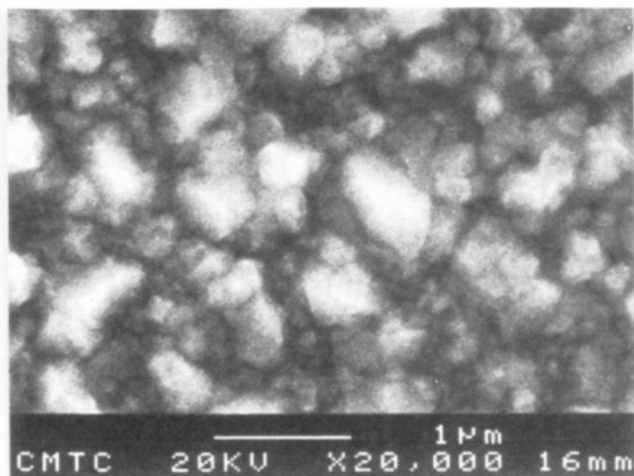
characteristic of polycrystalline copper (Figure 6, top). A slight preferred orientation in the (111) direction was observed since the peak intensity ratio  $I_{\text{Cu}(111)}/I_{\text{Cu}(200)}$  was equal to about 4, i.e., a factor of 2 higher than in the X-ray diffraction pattern of a randomly orientated powdery copper sample.

Typical Auger depth profiles of Cu, O, C, and Si atoms in the  $\text{Cu}-\text{SiO}_2-\text{Si}$  structures are given in Figure 6, bottom. The surface of the Cu films was slightly contaminated by carbon and oxygen. However, within the films, the content of C and O atoms was less than 1 at %. Accordingly, pure copper films were deposited by decomposition of  $\text{Cu}(\text{acac})_2$  in Ar- $\text{H}_2$  (1:1) gas mixtures.

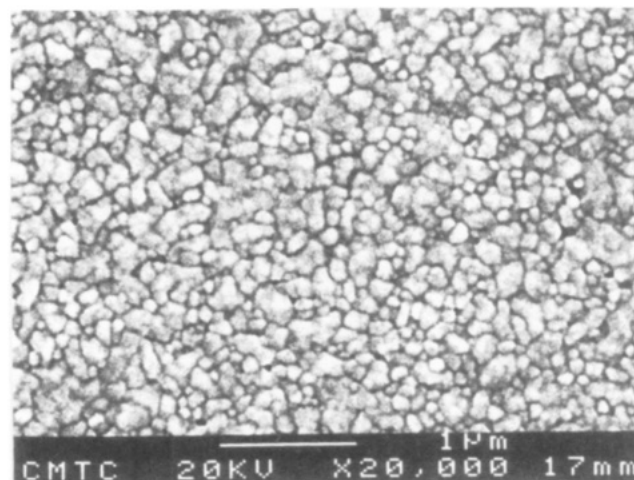
The morphology of copper thin films was characterized by scanning electron microscopy. The size of crystallites was found to depend on the deposition time, deposition

(31) Mehrotra, R. K.; Mehrotra, R. C. *Metal  $\beta$ -diketonates and allied derivatives*; Academic Press: New York, 1978.





**Figure 9.** Surface morphology of copper films deposited at 250 °C for 30 min in an H<sub>2</sub>-Ar (1:1) gas flow.

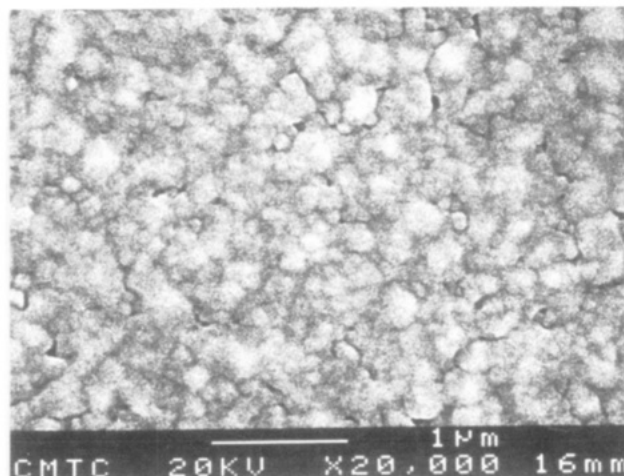


**Figure 10.** Surface morphology of copper films deposited at 225 °C for 20 min in an H<sub>2</sub>-Ar (1:1) gas flow.

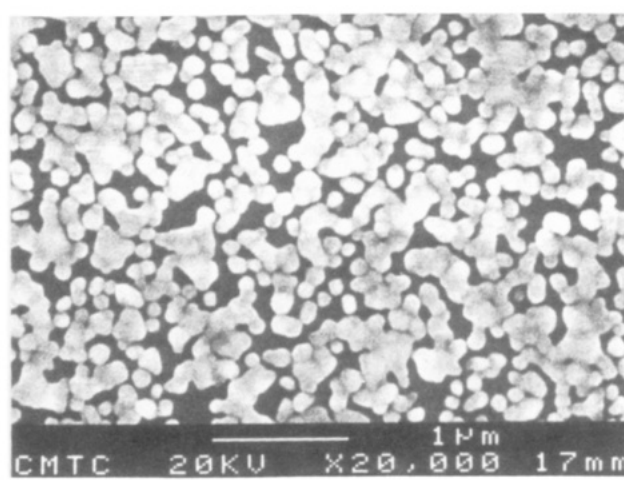
temperature, and composition of the gas phase. The surface morphology of copper films deposited in H<sub>2</sub>-Ar mixtures at 250 °C is shown in Figures 7-9. After 10 min of deposition, the copper film is composed of crystallites uniform in size (about 200 nm in diameter) separated by voids or cracks (Figure 7). The thickness of this film can be evaluated at about 200 nm, which is the value of the mean size of crystallites. In the films produced for longer deposition times (20 and 30 min), the distribution of the crystalline size broadens and the diameter of crystallites can reach 800 nm (Figures 8 and 9). In other words, the crystallite size increases with increasing film thickness.

The temperature effect on the structure of copper films is exhibited in Figures 8 and 10. The crystallite size is about 150 nm in the copper film deposited at 225 °C for 20 min. In addition, voids appear at the crystallite boundaries (Figure 10). The copper films produced at 250 °C for 20 min are composed of larger crystallites (Figure 8) resulting from either a higher deposition temperature or a larger film thickness. The voids or cracks are still observable in the film deposited at 225 °C for 30 min (Figure 11) although the film is about 30% thicker than the copper film shown in Figure 10.

The effect of the carrier gas composition on the structure of copper films is illustrated in Figures 11 and 12. The film deposited at 225 °C in pure hydrogen even after 30 min of deposition is composed of large islands separated by channels. This result shows that the nucleation rate and the growth rate of copper films decrease when the



**Figure 11.** Surface morphology of copper films deposited at 225 °C for 30 min in an H<sub>2</sub>-Ar (1:1) gas flow.



**Figure 12.** Surface morphology of copper films deposited at 225 °C for 30 min in a pure H<sub>2</sub> gas flow.

hydrogen pressure increases. This decrease in growth rate when using pure hydrogen as a carrier gas could result from the depletion in copper complex on the substrate surface due to a homogeneous nucleation process and volume reactions occurring in the gas phase.

### Conclusion

The results of the thermogravimetric study of the sublimation of Cu(acac)<sub>2</sub> indicate that the vapor pressure and sublimation rate of this copper complex compound are suitable in the range 140-190 °C for use Cu(acac)<sub>2</sub> as a CVD precursor. Successful CVD of pure copper films by decomposition of Cu(acac)<sub>2</sub> at low temperatures (220-250 °C) in pure H<sub>2</sub> or H<sub>2</sub>-Ar mixtures was demonstrated for the first time. Further experiments on CVD of copper films will be carried out by using H<sub>2</sub>-Ar mixtures at low pressures as a carrier gas in order to increase the sublimation rate of Cu(acac)<sub>2</sub> or reduce the temperature required for sublimation of the copper complex. Subsequent studies will be directed toward the CVD process and properties of the deposited material to determine the effects of CVD parameters on metal film characteristics.

**Acknowledgment.** We thank J. Garden of the Consortium for performing SEM examination of samples as well as Dr. G. Auvert and R. Pantel of C.N.E.T. for characterization of samples by Auger electron spectroscopy.

**Registry No.** Cu(acac)<sub>2</sub>, 13395-16-9; Cu, 7440-50-8; Si, 7440-21-3.