Thermal behaviour of CpCuPEt3 in gas phase and Cu thin films processing

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Abstract

Decomposition of CpCuPEt$_3$ (Cp=>>>(η5-C$_5$H$_5$)) and MOCVD of Cu films from CpCuPEt$_3$ have been investigated in the frame of an ongoing project on the processing of Cu-containing coatings. The behaviour of CpCuPEt$_3$ vapours under heating conditions was studied by in situ mass spectrometry. It was established that this compound is monomeric in gas phase. Its decomposition mechanism on hot surface was proposed. From mass spectroscopy experiments, it was established that decomposition in vacuum begins at 150 °C with evolution of PEt$_3$. Beyond 270 °C, formation of cyclopentadiene is observed, indicating that a change in decomposition mechanism occurs. The saturating vapour pressure of CpCuPEt$_3$ was estimated through static method, in order to optimize transport conditions and to control the molar fraction of the precursor in the gas phase. Finally, growth rate and microstructure of MOCVD processed Cu films from CpCuPEt$_3$ have been investigated.

1. Introduction

MOCVD of Cu has been widely studied, especially for the electrical properties of the films, due to its low resistivity (1.67 $\mu\Omega$ cm, bulk). Even if Cu can be deposited by alternative physical processes, MOCVD is the most studied one, due to the possibility of achieving conformal films and of selective deposition [1,2]. According to their chemical behaviour, the available organometallic copper CVD precursors can be divided into two main families: the copper (I) and the copper (II) complexes. The copper (II), especially β-diketonate derivatives, have been the most widely used [3,4]. The most common representative of this family is the bis hexafluoroacetylacetonate adduct Cu(hfa)$_2$, which leads to pure copper films in the 250 °C– 380 °C temperature range [5,6]. Copper (I) complexes, of general formula (X)Cu$^{(I)}L_n$, where L is a Lewis base, n=1,2, are volatile enough to be used in MOCVD processes. The ligand X is mainly a β-diketonate, but can be an alkoxide or a cyclopentadienyl ring, as the Lewis base L is often a phosphine or an olefin [7]. Another promising family of copper (I) amidinate has been recently proposed [8], used under H$_2$ reducing atmosphere.

If the aim of the CVD process is to produce pure copper films, the already well known β-diketonate Cu^I derivatives are appropriate precursors, as their vapour phase and thermal behaviours are well documented [3–7]. Nevertheless, if the overall objective of the process is to prepare oxygen-free complex phases, which may imply co-reaction or co-deposition with highly oxygen sensitive reactants, it is obvious that the use of the β-diketonate or alkoxide derivatives has to be avoided. In such a case, the oxygen-free complex CpCuPEt$_3$ can be selected as a good precursor candidate. It has been synthesized and characterized in the late fifties [9–11], but it has not been used as a MOCVD precursor before years [12,13]. More recently, it has been reported in Cu–Al co-deposition in combination with alanes [14,15]. In spite of the interesting potentialities of CpCuPEt$_3$ and related complexes as copper MOCVD precursors, little interest has been devoted to the investigations of their physical and thermal properties. For example, saturated vapour pressure of CpCuPEt$_3$ has been only estimated at 0.002 Torr at room temperature [12] and it will be shown thereafter that the proposed value is not correct. As we were interested in the optimization of the MOCVD processes for the deposition of metallic coatings

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which need the use of such oxygen-free precursors, we explored these interesting characterizations.

2. Experimentals

Thermal decomposition of the compound's vapours was studied by means of original mass spectrometric technique which is the combination of Knudsen effusion method with mass spectrometric measurements of gas phase composition. Details of this experimental technique have already been described [16]. We used input system for mass spectrometer imitating CVD reactor and automated system for data recording and processing. This allowed to record primary gaseous decomposition products in situ, as well as to determine temperature ranges in which they formed. The compound (<5 mg) in glass ampoule was placed into an evaporator and heated to a temperature (74 °C) when vapour pressure is enough that compound to be recorded by mass analyser. It should be noted that, due to the low pressure, decomposition of the precursor occurred on the walls of the reactor but not in the gas phase. Mass spectra were recorded at the energy of ionizing electrons of 70 eV. Saturating vapour pressures vs. temperature of CpCuPEt$_3$ have been obtained from a static method previously described [17].

MOCVD experiments were performed in a vertical cold wall reactor operating at 10 Torr. Experiments were conducted with CpCuPEt$_3$ heated either at 60 °C or at ca. 90 °C. Molar fraction of the precursor in the input gas was in the range 10^{-4}–10^{-3}. The substrates were stainless steel and silicon wafers. They were placed on a horizontal heating sample holder (58 mm diameter). The deposition temperature was in the range 158 °C–250 °C. The overall flow rate was 325 sccm (300 sccm N$_2$+ 25 sccm H$_2$). CpCuPEt$_3$ was purchased from Strem Chemical Inc., and purified by sublimation before use. Microscopy analysis was done using a LEO 435 VP SEM. The amount of deposited copper was determined by weighting the samples before and after experiments, using a Sartorius-Genius precision microscale. Stainless steel samples were degreased in absolute ethanol, in an ultrasonic bath, and dried under argon stream before use. The silicon wafers were degreased in a 70% H$_2$SO$_4$–
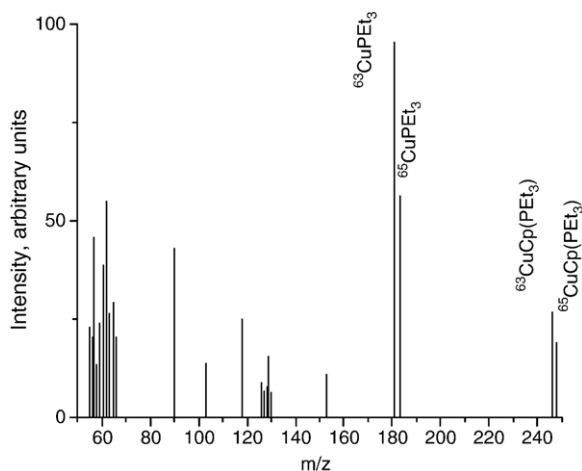
Fig. 2. Temperature dependence of intensity of ion peaks characterized the gas phase composition upon thermal decomposition of CpCuPEt$_3$.

30% H$_2$O$_2$ solution, rinsed with osmosed water and dried under argon stream before use.

3. Results and discussion

3.1. Mass spectrum of CpCuPEt$_3$

The mass spectrum of CpCuPEt$_3$ is shown in Fig. 1. There is no peak in mass spectra exceeding m/z of molecular ion. This indicates that the compound is monomeric in gas phase. The main fragmentation path under electron impact is well defined, with formation of [CuPEt$_3$]$^+$ ion (m/z 181 for ^{63}Cu isotope, the most intense) in mass spectrum. Its subsequent fragmentation results in the formation of the following ions [PEt$_3$]$^+$ (m/z 118), [HPEt$_2$]$^+$ (m/z 90), [H$_2$PEt]$^+$ (m/z 62), [HPEt]$^+$ (m/z 61). An important feature of the mass spectrum is the absence of ion peak corresponding to CuCp species that could be expected by analogy with (HFA)Cu(COD) [18].

3.2. Thermal decomposition of CpCuPEt$_3$ vapours

There are no changes in mass spectrum of the precursor under repeated heating and cooling cycles of the evaporator.
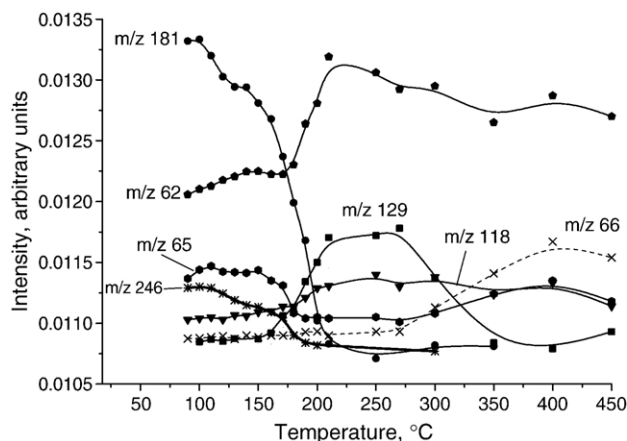
Fig. 1. Mass spectrum (m/z 50-250) of CpCuPEt$_3$ (EI 70 eV, 90 °C).
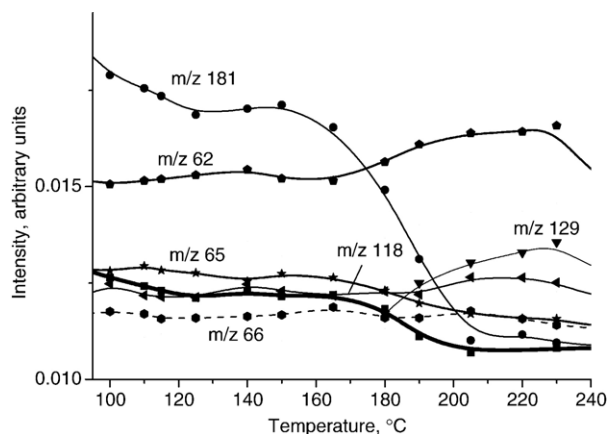
Fig. 3. Temperature dependence of intensity of ion peaks characterized the gas phase composition upon thermal decomposition of CpCuPEt$_3$ in the hydrogen.
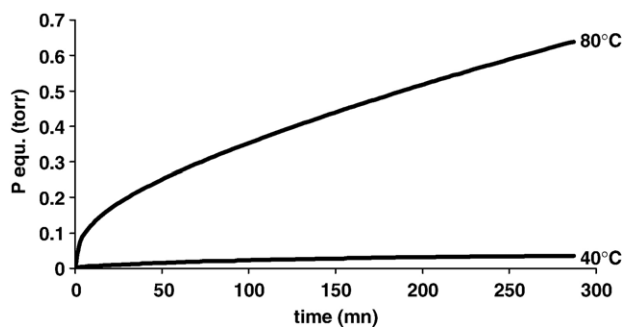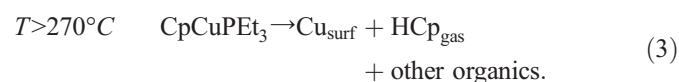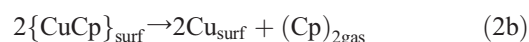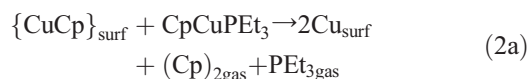
Fig. 4. Evolution of the pressure in the measurement chamber at 40 °C and 80 °C, showing the thermal decomposition of the precursor at 80 °C.

Fig. 5. Saturating vapour pressure of $CpCuPEt_3$ as a function of inverse temperature (diamonds: our data, square: Ref. [12]).

This reveals that $CpCuPEt_3$ presents sufficient vapourisation stability. In order to study thermal conversions, the compound's vapours were heated from 90 to 500 °C in vacuum and in the presence of hydrogen.

Temperature dependence of gas phase composition is presented in Fig. 2. We used decomposition temperature as an indication of thermal stability. This temperature was determined as the onset of the intensity decrease of the molecular peak and the intensity increase of products peaks. In vacuum it happens at 150 ± 10 °C.

Gaseous products of decomposition in vacuum are similar to those formed in the presence of hydrogen. The following molecular products: PEt_3 (m/z 118) with fragmentary ions (m/z 90, 62, 61), cyclopentadiene (m/z 66 with fragmentary ion m/z 65) and dicyclopentadienyl (m/z 130) with fragmentary ions (m/z 129, 128, 115, 103) are observed. It is difficult to be precise if radical product cyclopentadienyl Cp* (m/z 65) is formed upon decomposition due to the coexistence at this m/z of a fragmentary ion for cyclopentadiene. It should be noted that there are no copper-containing fragments like $CuPEt_3$, CuCp or $CuCp_2$ among the gaseous decomposition products. One can propose that such products are surface intermediates. Thus the scheme of thermal decomposition on the surface can be presented as follows:

$$T>150°C \quad CpCuPEt_3 \rightarrow \{CuCp\}_{surf} + PEt_{3gas} \tag{1}$$

$$\begin{aligned}\{CuCp\}_{surf} + CpCuPEt_3 &\rightarrow 2Cu_{surf} \\ &+ (Cp)_{2gas} + PEt_{3gas}\end{aligned} \tag{2a}$$

$$2\{CuCp\}_{surf} \rightarrow 2Cu_{surf} + (Cp)_{2gas} \tag{2b}$$

$$T>270°C \quad \begin{aligned}CpCuPEt_3 &\rightarrow Cu_{surf} + HCp_{gas} \\ &+ \text{other organics.}\end{aligned} \tag{3}$$

We believe that $CpCuPEt_3$ decomposes at heating with the formation of surface intermediate $\{CuCp\}_{surf}$ and evolution of PEt_3 in gas phase (Eq. (1)). Surface intermediate $\{CuCp\}_{surf}$ rapidly converts into Cu and Cp_2 by two possible ways (Eqs. (2a) and (2b)). Thus all decomposing particles produce copper film. Above 270 °C, formation of cyclopentadiene HCp is observed indicating that a change in decomposition mechanism occurs (Eq. (3)).
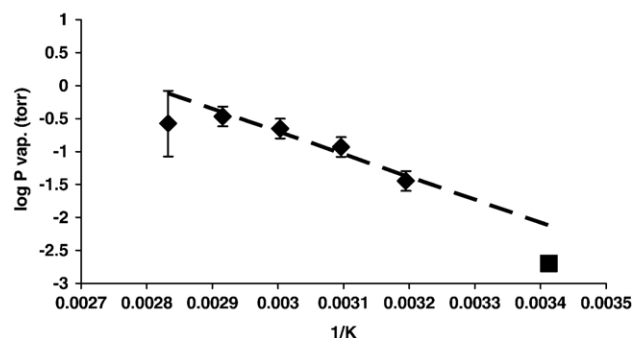
The main difference between decomposition in vacuum and in hydrogen is the increase of the thermal stability of the compound in the latter case. As it is shown in Fig. 3, decomposition in hydrogen is initiated at 170 ± 10 °C, to be compared with the previously determined onset temperature of 150 °C. The possible reason for this is competition between hydrogen and precursor molecules for adsorption places on the surface.

3.3. Vapour pressure determination

In order to define the transport conditions of the copper precursor, we have determined its saturating vapour pressure (P_{vap}), in the range 40 °C–80 °C. As concluded from the evolution of P_{vap} as a function of time in different temperatures, the complex is rather stable up to 70 °C. Noticeable decomposition occurs at 80 °C, as it is not possible to get a stabilized pressure in the measurement chamber (Fig. 4). Consequently, it was not attempted to measure the vapour pressure above 80 °C, and the value at 80 °C was not used for the estimation of the Clapeyron law, which can be written as: $\log P_{vap}$ (Torr) = 9.671 − 3455/K. Fig. 5 presents experimentally obtained values of P_{vap} at five different temperatures (diamonds in Fig. 5). Our data are in the same range as one data already reported in the literature [12] (square in Fig. 5). At 60 °C, the estimated saturating vapour pressure of $CpCuPEt_3$ is ca. 0.2 Torr, and is quite sufficient to ensure precursor transport in a MOCVD process operating under reduced pressure. If we assume that the gas phase saturation can be achieved in the sublimation device
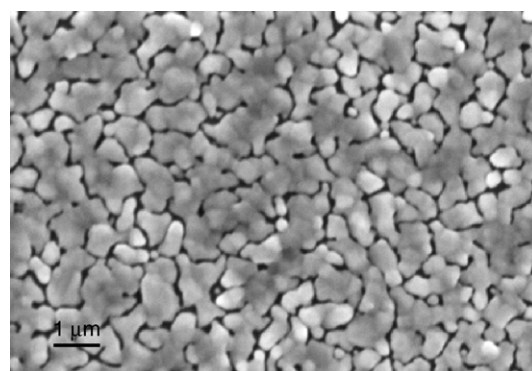

Fig. 6. SEM image of a copper film elaborated at 210 °C on stainless steel.
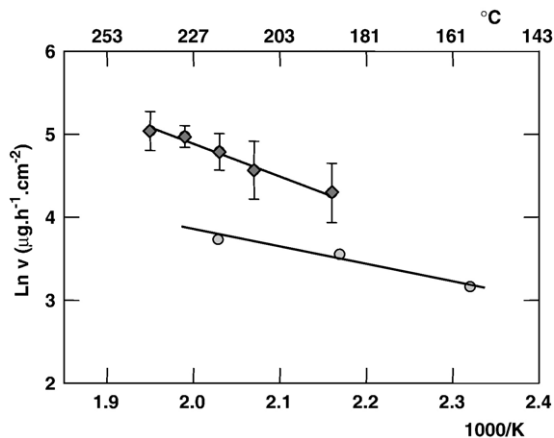
Fig. 7. L_n of growth rate vs. 1000/K on stainless steel (upper trace: sublimation temperature: 90 °C, lower trace: sublimation temperature: 60 °C).

of the MOCVD experiment, we can expect, for an overall pressure of 10 Torr and a carrier gas flow rate of 100 sccm, a maximum flow rate of CpCuPEt$_3$ as high as $\approx$ 2 sccm (1.3 g/h).

3.4. MOCVD experiments

Fig. 6 presents a SEM surface micrograph of a film deposited at 210 °C for 3 h. It is characterized by a nodular morphology which is characteristic of a Wolmer–Weber type of growth. EDS analysis of the films showed no contamination with carbon or phosphorus. The Arrhenius plot of copper growth rate on stainless steel is presented in Fig. 7 for the two sublimation temperatures investigated; i.e. ca. 90 °C and 60 °C (upper and lower set of data points, respectively). A slight increase of the growth rate can be observed for both conditions in the temperature range between 158 °C and 240 °C. Also, increase of the precursor concentration in the input gas through the increase of the sublimation temperature yields increase of the growth rate. These two results refer to a diffusion limited regime in these conditions. These results are in agreement with literature reports [19]. Together with a similar investigation of the MOCVD of Al, they are necessary for the forthcoming investigation of the co-deposition of Al–Cu.

4. Conclusion

CpCuPEt$_3$ has sufficient vapourisation stability up to 75 °C and relatively low thermal stability to be used as precursor for MOCVD of copper films in the 150–290 °C temperature range.

From the suggested mechanism it can be concluded that decomposition proceeds by the way being favourable for no carbon and phosphorous impurities incorporation into the copper film. Saturating vapour pressure determinations have shown that CpCuPEt$_3$ is quite stable below 70 °C, the Clapeyron law has been established in the 40 °C–70 °C range, and can be written as: log P_{vap} (Torr) = 9.671–3455/K. MOCVD experiments produced nodular high purity copper films, under a diffusion limited regime. It is concluded that CpCuPEt$_3$ is a suitable precursor for copper MOCVD, even if its thermal fragility should make it used below 70 °C.

Acknowledgements

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