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THERMAL ANALYSIS OF METALORGANIC COMPLEXES OF COPPER FOR EVALUATION AS CVD PRECURSORS

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Abstract

Metalorganic complexes of copper have been synthesized by modifying the ligand in the β-diketonate class of compounds. Detailed thermal analysis of several β-diketonate complexes of copper has been carried out to evaluate their suitability as precursors for chemical vapor deposition (CVD). A comparison of their relative volatilities has been made by determining their sublimation rates at different temperatures. Thermal analyses of these complexes reveal significant differences among their volatilities and decomposition patterns.

Keywords: CVD, metalorganic precursors, thermogravimetry

Introduction

CVD is a process for the synthesis of thin films in which its constituents are transported in the vapor phase to the deposition zone where the growth of the film of the desired material occurs following chemical reaction(s) on a heated substrate [1]. Compared to other film deposition methods, CVD offers several advantages such as high deposition rates and conformal coverage. Metalorganic precursors for CVD must display a number of important physical and chemical properties which include sufficient volatility, availability in significant quantities with the required purity, low toxicity, and ligand stability such that clean metal-ligand dissociation is possible at the substrate temperature [2].

In view of its potential application in the metallization of VLSI circuits, major effort has been undertaken recently to develop a low-temperature, high-rate CVD process for copper. As a result, a wide variety of Cu(I) and Cu(II) metalorganic compounds have been tried as precursors for copper CVD [3]. The Cu(I) precursors are quite volatile and lead to low deposition temperatures, but are relatively unstable. The Cu(II) precursors are stable, but have lower volatility and require higher deposition temperatures. Ligand-stabilised Cu(I) hexafluoro-

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acetylacetonates (hfac) and Cu(II)(hfac)$_2$ have led both to high rates of deposition and to significantly lower deposition temperatures [3]. However, fluorination makes precursor-handling more difficult, which it is desirable to avoid. Additionally, hfac-based Cu(I) precursors, even when ligand stabilized, have poor thermal characteristics and short shelf life [4]. The ideal choice of a precursor for CVD of Cu could be a copper complex with high vapor pressure and stability, as well as low temperature for copper deposition, without fluorination. We aimed our study at developing Cu(II) precursors with these properties.

The objective of this work has therefore been to study the effect of the variation of the terminal groups of the β-diketonate complexes of copper on their volatility, thermal stability and decomposition. Several studies published in the literature address the issue of stability of the β-diketonate class of metal complexes, but have been limited to thermal, IR and mass spectrometric analyses of some of the precursors used in the CVD of cuprate superconductors [5, 6].

By varying the terminal groups of the ligand, we have synthesized three Cu(II) precursors which may be regarded as modifications of either bis(acetylacetonato)Cu(II) or of bis(dipivaloylmethanato)Cu(II) [abbreviated as Cu(acac)$_2$ and Cu(dpm)$_2$, respectively]. The ligands considered were t-butylacetoacetate (tbaoac), methylacetoacetate (meaoac), and ethylacetoacetate (etaoac), each of which has an ester group β to the carbonyl group. The molecular structures of Cu(acac)$_2$ and Cu(dpm)$_2$ and those of the modified complexes, bis(t-butylacetoacetato)copper(II) or Cu(tbaoac)$_2$, bis(methylacetoacetato)copper(II) or Cu(meaoac)$_2$, and bis(ethylacetoacetato)copper(II) or Cu(etaoac)$_2$ are shown in Fig. 1. In these modified complexes, the presence of electronegative oxygen may be expected to produce a more repulsive shell around the complex, reducing the strength of metal-oxygen bonding and thereby increasing the volatility. The presence of oxygen in the ligand is expected to trigger a decomposition pathway such that the pyrolysis temperature for copper deposition is reduced. The synthesis of the precursor Cu(tbaoac)$_2$ and the deposition of Cu films using it have been reported [7].

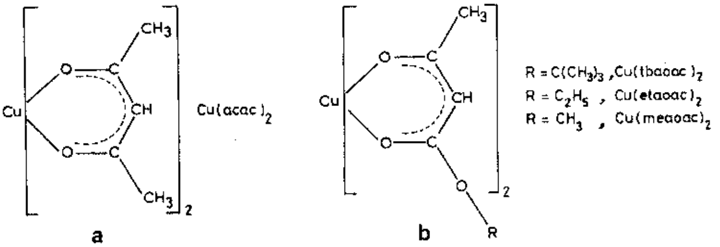

Fig. 1 Molecular structures of the metalorganic precursors of copper

Thermogravimetric and differential thermal analyses (TG/DTA) can be used as powerful tools in comparing the relative volatilities and thermal stabilities of different metal β-diketonate chelates [8]. By examining the thermograms, it is possible to follow the changes in volatility due to the substitution of various chemical groups in the ligand. Thermal analysis is also required to optimize the temperature at which the precursor vaporizer should be maintained during CVD. TG/DTA was carried out on samples taken from each batch of the precursors synthesized, to ensure that they all had identical thermal behavior, i.e., thermal analysis was employed as the primary tool in verifying batch-to-batch reproducibility of the synthesis procedure. TG was also employed to verify that precursors did not deteriorate over a period of several months while being stored in an evacuated desiccator. In this paper, we report on the use of thermal analysis as an effective tool for the characterization of copper complexes eventually used as precursors for the CVD of copper.

Experimental

The copper complexes $Cu(acac)_2$ and $Cu(dpm)_2$ were prepared by modifying the procedure reported in the literature [9]. $Cu(tbaoac)_2$, $Cu(etaoac)_2$, and $Cu(meaoac)_2$ were synthesized by chelating, respectively, the ligands tert-butylacetoacetate, ethylacetoacetate, and methylacetoacetate with a copper salt under ice-cold conditions. The complexes were then recrystallized to obtain high purity single crystals of these materials. Typically, 20 gms of a given complex were synthesized. The precursors were characterized by melting point determination, elemental analysis, IR spectroscopy, mass spectrometry, and X-ray diffraction. The molecular weight and the melting points of the copper complexes are tabulated in Table 1. The thermal characteristics of the compounds relevant to their suitability as precursors for CVD were studied by simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA). The thermal analyses (TG/DTA) were carried out using a simultaneous thermal analyzer (STA 1500, Polymer Laboratories). About 10 mg of the finely powdered sample was placed in the sample pan and its temperature was raised at a programmed heating rate of 10°C min^{-1}. All analysis was carried out in a flowing high purity argon ambient. The mass lost by the sample and the differential thermal signal were recorded as a function of temperature. Thermogravimetry was also used to determine the sublimation rates of the various precursors as a function of temperature. This was done by recording the mass of the sample as a function of time after equilibrating the sample temperature at a chosen value. The measured sub-

Table 1 Melting point (MP) and molecular weight (MW) of the copper precursors

Precursor	MP/°C	MW
$Cu(acac)_2$	235	262
$Cu(dpm)_2$	194	429
$Cu(tbaoac)_2$	110	377
$Cu(etaoac)_2$	192	321
$Cu(meaoac)_2$	170	294

limation rates are expressed as the mass lost by the sample per min per unit initial mass of the sample (mg/min/mg). As the sublimation rate is a function of the total surface area, care was taken to ensure that the samples were powdered to have the same average grain size each time.

Results and discussion

The thermal analysis data for Cu(acac)$_2$ and Cu(dpm)$_2$ are shown in Figs 2 and 3 respectively. Cu(acac)$_2$ begins to sublime and lose mass at about 150°C, with the mass loss being complete by about 245°C, no residue being left in the sample crucible. The sharp endotherm at 235°C corresponds to the melting point of Cu(acac)$_2$, and is in agreement with the data in Table 1. The thermal behaviour of Cu(dpm)$_2$ is similar, except that it begins to sublime and lose mass at 140°C, noticeably lower than for Cu(acac)$_2$. The melting point (194°C) is in accordance with that determined by the capillary method (Table 1). The sublimation is complete by 250°C, no residue being left. This is significantly lower than 350°C where Cu(dpm)$_2$ decomposes [10], so that the decomposition is not recorded in the TG/DT analysis.

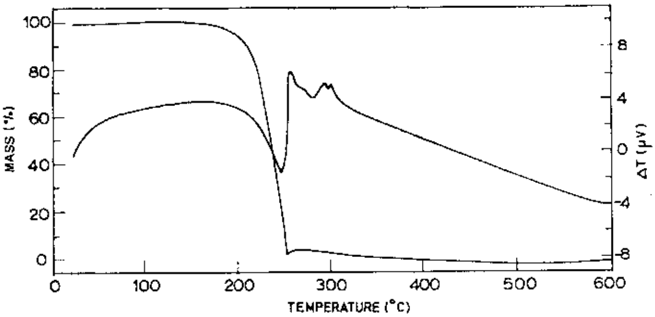

Fig. 2 Simultaneous TG/DTA of Cu(acac)$_2$

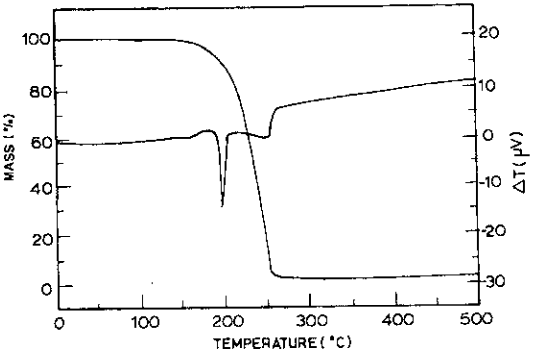

Fig. 3 Simultaneous TG/DTA of Cu(dpm)$_2$

It is apparent from the TG data as well as from sublimation rate measurements (given below) that $Cu(dpm)_2$ is more volatile than $Cu(acac)_2$. One of the factors that contribute to the higher volatility of $Cu(dpm)_2$ is the presence of bulky tertiary butyl groups at the terminals of the dpm ligand (Fig.1). Such bulky groups weaken the intermolecular van der Waals interactions, raising volatility. By contrast, the acac ligand is terminated by methyl groups which, being less bulky, allow for greater intermolecular interaction. This evidenced by the presence of $Cu_2(acac)_3$ in the mass spectrum of $Cu(acac)_2$, indicating that oligomerisation takes place, leading to reduced volatility [11]. Mass spectra show that such oligomerisation does not occur in $Cu(dpm)_2$, supporting the contention that bulky terminal groups contribute to enhanced volatility [11].

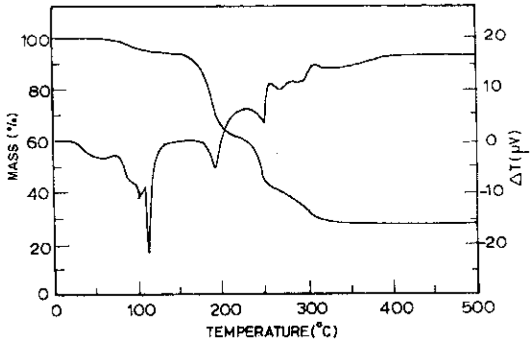

Fig. 4 Simultaneous TG/DTA of $Cu(tbaoac)_2$

The TG/DTA data for the acetoacetato complexes (ketocarboxylates) are shown in Figs 4–6. It is apparent at once that the mass loss patterns for these three Cu(II) precursors are more complex than in Figs 2 and 3, and do not show a monotonic mass loss as temperature is raised. Moreover, the mass loss is not total, even when the sample temperature is raised to as much as 600°C. The DTA patterns comprise peaks of different sizes, and correspond to inflexion points in the TG curves. The most complex behaviour is that of $Cu(tbaoac)_2$ (Fig. 4) , which begins to sublime at 90°C, which is much lower than the corresponding temperatures of $Cu(acac)_2$ and $Cu(dpm)_2$. In addition to the loss of water of crystallization at about 100°C, the DTA signal also marks the melting that occurs at 110°C (Table 1). The compound begins to decompose at a relatively low temperature of 190°C, but the decomposition is complex, with the TG/DTA data showing different stages of decomposition near 190, 248 and 304°C. It would be necessary to carry out evolved gas analysis or *in situ* mass spectrometry to elucidate the details of the various stages of decomposition. The mass loss is not total, with the residue stabilizing beyond 350°C at about 22% of the original mass. This is larger than 16.1% which corresponds to the proportion of copper in the starting material, including the water of crystallization [12]. The residue may be CuO, which would amount to 20.1% of the original mass. CuO is the more stable of the oxide phases of copper at temperatures exceeding 400°C. The low temperature at which Cu(tbaoac)$_2$ begins to decompose indicates that, as desired, the deposition of Cu from this complex may be possible at a relatively low temperature.

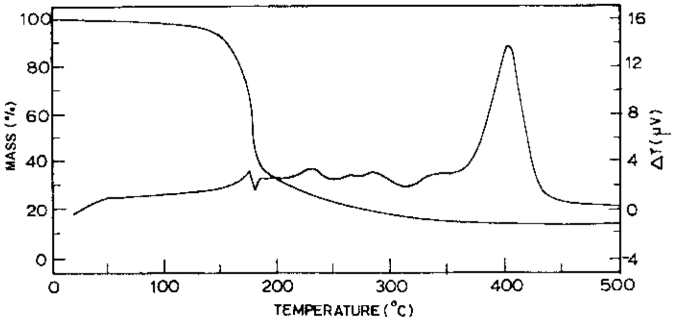

Fig. 5 Simultaneous TG/DTA of Cu(etaoac)$_2$

Figure 5 shows the TG/DTA data for Cu(etaoac)$_2$. The TG curve indicates that a large portion of the compound sublimes below 200°C. The TG profile can be divided into two temperature regions, (i) mass loss from 97–30% of the original mass between 170–230°C, (ii) mass loss from 30–22% of the original mass between 320–450°C. This staggered mass loss can be attributed to two phenomena, sublimation and thermal decomposition. The TG curve levels off at 20% of the original sample mass, which is close to the initial copper content (19.8 wt.%) of Cu(etaoac)$_2$. The DTA curve showed an endotherm at 192°C which corresponds to the melting point of Cu(etaoac)$_2$. The broad exotherm at 380°C corresponds to the decomposition of Cu(etaoac)$_2$.

Figure 6 shows the TG/DTA results of Cu(meaoac)$_2$. The precursor begins to sublime at a temperature as low as 35°C and, in the region 100–180°C, suffers a mass loss from 95 to 65% of the original mass. There is a further mass loss from 65 to 35% of the original mass in the temperature range 180–380°C. A residue of about 35% of the original mass was left behind in the crucible which is greater than the initial copper content (21.3 wt.%) in Cu(meaoac)$_2$. If CuO were formed the residue would have amounted to 27% of the original sample mass. The DTA

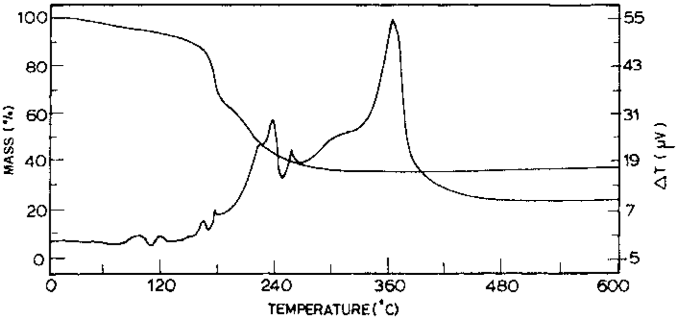

Fig. 6 Simultaneous TG/DTA of Cu(meaoac)$_2$

results show an endotherm at 170°C which corresponds to the melting point of Cu(meaoac)$_2$. Two exotherms were observed at 240 and 335°C, which correspond to the decomposition of Cu(meaoac)$_2$.

In a CVD process where precursors are solid materials, the sublimation rate of the precursor in the flowing carrier gas ambient actually determines the rate of precursor delivery into the reactor. The sublimation rate of a solid precursor is easier to determine and more useful for developing a CVD process than a knowledge of the equilibrium vapor pressure at a given temperature. Using the TG analyser, a detailed study was conducted to determine the mass loss of the complex as a function of time at different sublimation temperatures. Specifically, this was done by first equilibrating the sample at the desired temperature and subsequently recording the mass loss as a function of time. To keep the surface area constant in all experiments, the sample crucible was densely filled each time with fine powder of the precursor of nearly the same initial mass (~10 mg). All experiments were carried out under flowing argon (40 sccm) environment.

Figure 7 shows the results of a comparative study of the sublimation of Cu(acac)$_2$, Cu(dpm)$_2$, Cu(tbaoac)$_2$, Cu(etaoac)$_2$ and Cu(meaoac)$_2$ at 120°C. The data were recorded after the sample temperature had stabilized. The constant slopes of the mass loss *vs.* time plots show that the sublimation rates of the precursors are constant over lengths of time similar to those involved in a typical film deposition run employed in this study, except for Cu(meaoac)$_2$ where the sublimation rate drops after about 100 min. The constancy of sublimation over prolonged periods (at a given temperature) is essential for to obtain reproducibility of growth runs and for scaling up of a CVD process where a solid precursor is used. It was observed that Cu(tbaoac)$_2$ has the highest sublimation rate among the Cu(II) precursors prepared in this study.

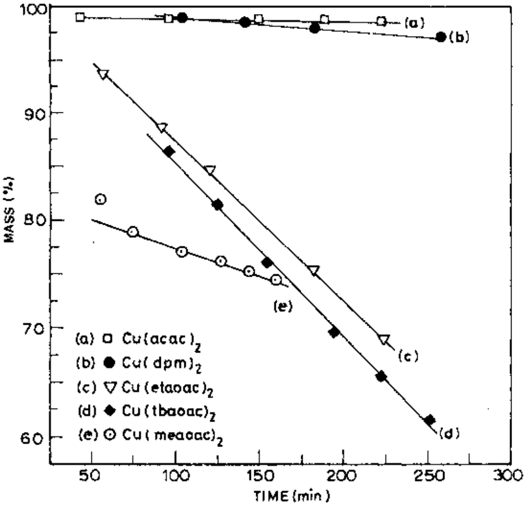

Fig. 7 Mass loss as a function of time at 120°C for (a) Cu(acac)$_2$, (b) Cu(dpm)$_2$, (c) Cu(tbaoac)$_2$, (d) Cu(etaoac)$_2$, and (e) Cu(meaoac)$_2$

Table 2 Activation energy for precursor sublimation

Precursor	Activation energy/kJ mol^{-1}
$Cu(acac)_2$	122.1
$Cu(dpm)_2$	104.9
$Cu(meaoac)_2$	66.4
$Cu(etaoac)_2$	53.4
$Cu(tbaoac)_2$	50.4

Figure 8a shows the Arrhenius plot of the sublimation rate of $Cu(acac)_2$ and $Cu(dpm)_2$ and Fig. 8b shows the corresponding plot for $Cu(tbaoac)_2$, $Cu(etaoac)_2$ and $Cu(meaoac)_2$. It is seen that the sublimation rate of $Cu(tbaoac)_2 > Cu(etaoac)_2 > Cu(meaoac)_2 > Cu(dpm)_2 > Cu(acac)_2$. The activation energy for sublimation of each of the precursors is tabulated in Table 2. It is found that $Cu(tbaoac)_2$ has the lowest activation energy and $Cu(acac)_2$ has the highest activation energy.

It is thus established experimentally that the Cu(II) compounds containing keto ester ligands have higher sublimation rates (over the range of temperatures 90–150°C compared to $Cu(acac)_2$ and $Cu(dpm)_2$). The higher sublimation rates at low temperatures in the range 90–150°C may be attributed to the presence of electronegative oxygen in the ligand which produces a more repulsive shell around the complex, reducing the strength of the metal oxygen bond and thereby increasing the volatility. Among the three ketocarboxylates, the sublimation rate (volatility) is in the order $Cu(tbaoac)_2 > Cu(etaoac)_2 > Cu(meaoac)_2$, i.e., the volatility is greater when the terminal groups in the ligands are bulkier. This is in accord with the premise, stated above, with which the precursors were selected.

The higher volatility of $Cu(dpm)_2$ compared to $Cu(acac)_2$ can be understood in a similar manner, because the methyl groups that terminate the latter are replaced in the former by the bulkier t-butyl groups, leading to reduced strength of the intermolecular van der Waals interaction, and hence to increased volatility. A similar trend in volatility of Cu(II) β-diketonates has been reported earlier [13]. It is thus possible to understand the observed order in the volatility of the five Cu(II) compounds, i.e., $Cu(tbaoac)_2 > Cu(etaoac)_2 > Cu(meaoac)_2 > Cu(dpm)_2 > Cu(acac)_2$.

A comparison of the sublimation rates of the different precursors under conditions of actual use is instructive. The least volatile of the Cu(II) complexes, $Cu(acac)_2$, has a sublimation rate of 1.35×10^{-4} mg/min/mg at 140°C, which compares with the sublimation rate of 3.99×10^{-4} mg/min/mg for $Cu(dpm)_2$ at 130°C. This threefold difference in precursor volatility may not translate directly into a similar increase in the deposition rate in a CVD process, which depends on the details of the chemical reactions involved. Yet, higher volatility means that the vaporizer and the precursor transport lines can be maintained at lower temperatures (and still prevent vapor condensation), which is generally desirable. The precursor $Cu(tbaoac)_2$ is considerably more volatile, with a sublimation rate of 8.25×10^{-4} mg/min/mg at 100°C. Compared to $Cu(tbaoac)_2$, $Cu(etaoac)_2$ is somewhat less volatile, and the sublimation rate of $Cu(meaoac)_2$ was markedly lower than that of $Cu(etaoac)_2$ under similar conditions.

For practical use as a CVD precursor, the sublimation (vaporization) rate at the chosen temperature must be steady over periods of time involved in typical CVD growth runs, i.e., 2–3 h. Sublimation data gathered for $Cu(dpm)_2$,

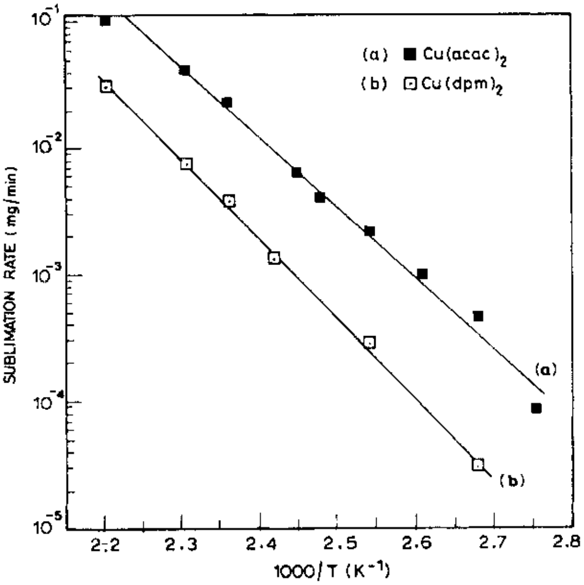

Fig. 8a Sublimation rate as a function of temperature for (a) $Cu(acac)_2$ and (b) $Cu(dpm)_2$, (argon flow rate=40 s cm^3)

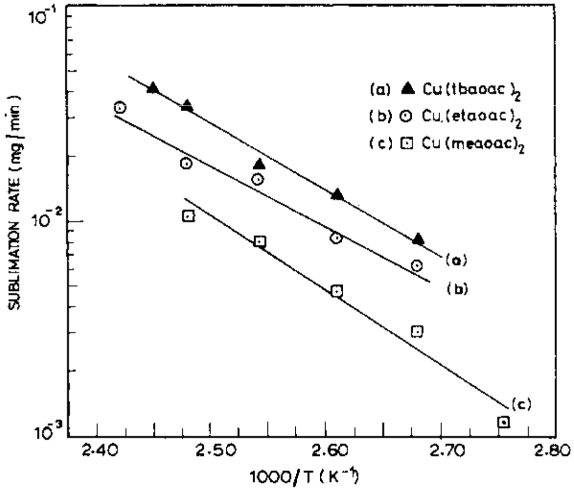

Fig. 8b Sublimation rate as a function of temperature for (a) $Cu(tbaoac)_2$, (b) $Cu(etaoac)_2$, and (c) $Cu(meaoac)_2$

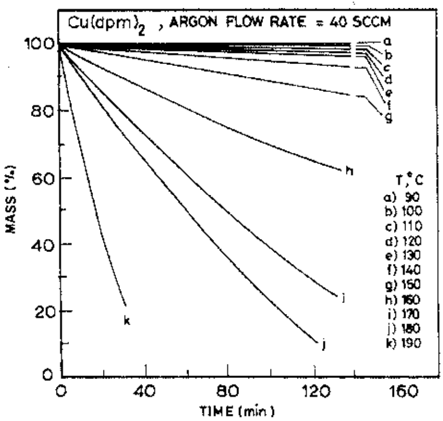

Fig. 9 Mass loss as a function of time at different temperatures for Cu(dpm)$_2$

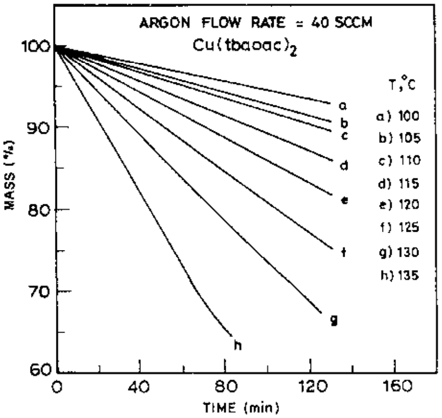

Fig. 10 Mass loss as a function of time at different temperatures for Cu(tbaoac)$_2$

Cu(tbaoac)$_2$, and Cu(etaoac)$_2$ as a function of time, but for different sublimation temperatures are shown in Figs 9–11 respectively. It is seen that, for the complexes Cu(dpm)$_2$ and Cu(tbaoac)$_2$, the mass lost by the sample due to sublimation is remarkably constant over long periods of time and over a wide range of sublimation temperatures. This indicates strongly that the growth rate of films produced by CVD from these complexes would be constant, making for a predictable growth process. This is of practical importance because CVD lacks the facility for *in situ* growth rate monitoring that is possible in physical vapor deposition (PVD) processes. It may also be seen from Fig. 11 that, when the sublimation temperature (140°C) is high, the sublimation rate is no longer constant in time. This is possibly because the 'sintering' that takes place at higher temperature increases the average grain size and reduces the total surface area of the sample, thus reducing the sublimation rate. By contrast, the sublimation rate of

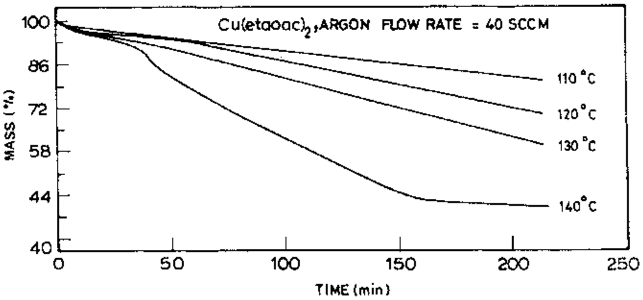

Fig. 11 Mass loss as a function of time at different temperatures for Cu(etaoac)$_2$

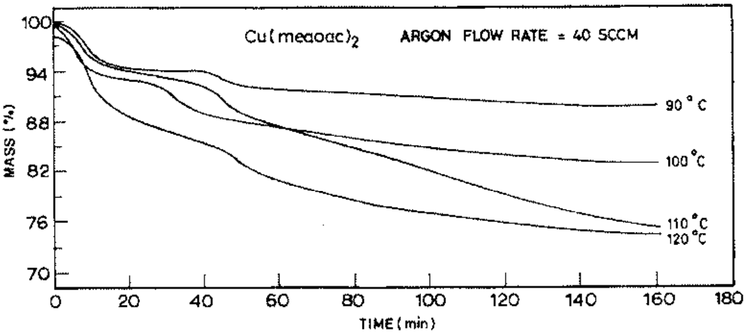

Fig. 12 Mass loss as a function of time at different temperatures for Cu(meaoac)$_2$

Cu(meaoac)$_2$ (Fig. 12) is not constant regardless of the sublimation temperature. The reason for this is not apparent, but the use of Cu(meaoac)$_2$ as a CVD precursor is likely to lead to unsteady growth rates.

The CVD of copper was carried out using Cu(dpm)$_2$, Cu(tbaoac)$_2$, and Cu(etaoac)$_2$, using hydrogen as the carrier gas. It was found that the threshold temperature for film deposition was 275°C from Cu(dpm)$_2$, 225°C with Cu(etaoac)$_2$, and 185°C with Cu(tbaoac)$_2$ [11]. This is consistent with the expectation that the facile decarboxylation in the two latter precursors would lower the temperature for Cu deposition. That the threshold temperature for deposition from Cu(tbaoac)$_2$ is lower than from Cu(etaoac)$_2$ is explained by the relative bulk of the t-butyl group. Thus, by tailoring the precursor Cu(acac)$_2$, it has been possible to lower the threshold temperature for Cu deposition by CVD in a predictable manner.

Summary

The synthesis and characterization of several Cu(II) precursors have been carried out. Cu(tbaoac)$_2$, Cu(etaoac)$_2$ and Cu(meaoac)$_2$ were prepared by modifying the ligand acac with a view to increasing the sublimation rates and lowering the pyrolysis/decomposition temperature, without fluorination of the ligand. It can be inferred from the TG/DTA data that $Cu(acac)_2$ is less volatile than $Cu(dpm)_2$. The presence of t-butyl groups in the ligand in $Cu(dpm)_2$ is one of the factors that contribute to the enhancement in volatility. In the case of $Cu(tbaoac)_2$, $Cu(etaoac)_2$ and $Cu(meaoac)_2$, the presence of electronegative oxygen in the ligand produces a more repulsive shell around the complex reducing the strength of the metal-oxygen bond and thereby increases the volatility. From the sublimation studies it is observed that $Cu(tbaoac)_2$ has the highest sublimation rate and at a given temperature the sublimation rates decreases in the following order. $Cu(tbaoac)_2 > Cu(etaoac)_2 > Cu(meaoac)_2 > Cu(dpm)_2 > Cu(acac)_2$. The sublimation rates are constant over a period of time (60–120 min). From the TG/DTA data, it can also be inferred that $Cu(tbaoac)_2$ has a lower decomposition temperature than $Cu(etaoac)_2$ and $Cu(dpm)_2$. Thus, $Cu(tbaoac)_2$ is expected to have a lower threshold temperature for copper deposition by CVD and this was experimentally observed when CVD of Cu was attempted using these precursors. Thus, thermal analysis can be used as an effective tool for characterizing solid precursors for CVD.

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