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Comparative study of copper deposits obtained by thermal decomposition and photo-assisted chemical vapour deposition of 3-diketonate complexes

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Abstract : The use of the $\text{Ba}(\text{thd})_2$ precursor, in the elaboration of thin superconductor layers by OMCVD, is not satisfactory because its volatility decreases when it is kept at the sublimation temperature during the deposition. In order to avoid this problem, fluorine complexes, such as $\text{Ba}(\text{hfa})_2$ can be used. Nevertheless, its thermal decomposition at high temperature induces the presence of baryum fluoride, which is harmful for obtaining superconductor films with high critical temperature. This work is aiming to study the elaboration of superconducting deposits at low temperature and without fluorine. We have undertaken a program based on a photo-assisted thermal decomposition of various organometallic compounds, which are used as precursors of superconductor layers. Photonic assistance enables to obtain copper deposits at 150°C. The results of the photo-assisted decomposition of $\text{Cu}(\text{thd})_2$ and $\text{Cu}(\text{hfa})_2$ are presented here.

1.-Introduction :

The elaboration of superconducting YBaCuO layers from thermal decomposition of organometallic(OM) precursors has been reported at relatively high temperatures of about 850°C (1) and at relatively low temperatures of about 580°C (2). The most used OM precursors of Cu, Y and Ba are $\text{Cu}(\text{L})_2$, $\text{Ba}(\text{L})_2$ and $\text{Y}(\text{L})_3$, where L represents the diketonate ligand having the general formula $\text{R}_1\text{-CO-CH-CO-R}_2$. According to the nature of R_1 and R_2 the OM volatility changes. Particularly, the complex $\text{Ba}(\text{thd})_2$ (where thd represents the 2,2,6,6-tetramethyl-3,5- heptanedionate) has a low volatility. Moreover this volatility decreases as a function of the time when the precursor $\text{Ba}(\text{thd})_2$ is kept for a long time (around 30min) at the sublimation temperature (220°C). On the other hand, the use of fluorinated ligands such as 1,1,1,5,5,5-hexafluoroacetylacetonate in place of hydrogenated ones improves and regulates the volatility. A mass spectrometry investigation of the gaseous phase coming from the sublimation of $\text{Ba}(\text{thd})_2$ (3) and $\text{Ba}(\text{hfa})_2$ permits to follow the variation of volatility. According to these results, the fluorinated compound appears suitable for CVD experiments. However, the thermal decomposition at

about 650°C-900°C leads to the presence of barium fluoride (BaF_2) in the films. In order to avoid the formation of this very stable compound, it is necessary to work at low temperature.

In order to achieve this objective we have undertaken a program to lower the decomposition temperature using UV -assistance and to compare the thermal behaviour of various OM compounds when the chemical reaction occurs with or without UV-irradiation. The initial experiments carried out in our laboratory concerning the elaboration of copper films from $\text{Cu}(\text{thd})_2$ and $\text{Cu}(\text{hfa})_2$ are reported here.

2.-Experimental :

To study the influence of UV light on the decomposition of different precursors in a stainless steel cold wall reactor was used (Fig. 1). The substrate to be coated is heated by an electrical resistance whose temperature is controlled by a chromel/alumel thermocouple. The sublimator containing the copper complexes is heated at 140°C for the molecule A : $\text{Cu}(\text{thd})_2$ and at 55°C for the molecule B : $\text{Cu}(\text{hfa})_2$.

Fig. 1 - Schematic diagram of the photo-assisted CVD apparatus.

The carrier gas was helium, and its flow rate is regulated by a mass flow controller. All the lines leading from the sublimator to the reactor are maintained at sufficient temperature to avoid the condensation of the precursors.

The UV-irradiation used is provided by a low pressure Hg lamp (254-185 nm). Its irradiation passes through a suprasil window which is located in front of the substrate where the reaction occurs. The low pressure in the reactor is made by a pumping system.

The different experimental variables used are presented in table 1 and the chemical composition of the substrate (Al alloy) is given in table.2.

Table 1 : Experimental conditions used in deposition of copper films from molecule (A) and molecule (B).

Experimental factors	Molecule (A)	Molecule (B)
Sublimation temperature	140°C	55°C
flow rate (He)	30 sccm	30 sccm
pressure in reactor	10 torr	10 torr
substrate temperature	150°C - 390°C	300 - 350°C
UV lamp (17 mw/cm ²)	ON or OFF	ON or OFF

Table 2 : Chemical composition of the substrate

%	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
min	0.4		0.15		0.8	0.04			98.61
max.	0.8	0.7	0.40	0.15	1.2	0.35	0.25	0.15	96

The figure 2 shows the absorption spectrum of the Cu(thd)₂ complex dissolved in pure hexane. Three peaks located between 370 and 190 nm were observed, the widest peak has a shoulder. The assignment of the electronic transitions is presented in table 3.

Fig. 2 - UV absorption spectrum of hexane solution of Cu(thd)₂

Table 3 - UV absorption peak positions. Assignments are after the reference (4)

Band	202 nm	249 nm	298 (308) nm
assignment	Cu(3 dyz) $\longrightarrow$ π^*	$\sigma \longrightarrow$ Cu (3 dxy)	$\pi \longrightarrow \pi^*$

The thickness of the films was measured by mean of a profilometer (Talister type). The step was created by chemical etching with diluted (20 %) nitric acid. The solid deposits were analysed by XPS (VG ESCALAB MK II) using the $AlK\alpha$ X ray radiation.(1486.6 eV). The cristallinity of the films was investigated by X-ray diffraction and the chemical composition was determined by Energy Dispersive Spectroscopy (EDS). The surface morphology was examined by Scanning Electron Microscopy (SEM).

3.-. Results and discussion :

Without irradiation the minimum decomposition temperatures found for $Cu(thd)_2$ and $Cu(hfa)_2$ are in good agreement with the values reported earlier (5). Particularly at temperatures lower than 300°C for the molecule (A) we did not observe any coating. With the UV irradiation the decomposition temperature lowered to about 150°C.

The correlation between the surface morphology and the coating conditions (substrate temperature T_s , precursor nature, UV use) was investigated by SEM. The Fig.3 shows the surface morphology of copper films obtained from $Cu(thd)_2$ and $Cu(hfa)_2$ with and without UV irradiation at different temperatures. The films obtained from $Cu(thd)_2$ decomposed assisting with UV present a high density of little crystals (Fig. 3a, 3b, 3c), while the films deposited without UV are composed of greater grains (Fig. 3d).

The experiments carried out with UV assistance show that the temperature plays an important role on the sizes and the shapes of the grains. At 200°C thin platelets are displayed, while at 250°C we observe an evolution, and the coating is composed by little grains and columns. With $Cu(hfa)_2$ precursor, at the temperature of 350°C, we can observe a difference in film morphology for experiments with and without UV irradiation (Fig. 3e and 3f).

XPS analyses of films deposited from $Cu(thd)_2$ showed the presence of copper, carbon and oxygen. These two last elements are present as surface contaminants. They disappear by Ar^+ ion bombardment as shown in Fig. 4 a . Copper appears as the main element in the films.

For the films obtained from $Cu(hfa)_2$, it is interesting to follow the presence and the evolution of the fluorine signal. For example at 350°C, the XPS spectra of the surface of films elaborated with or without UV-irradiation show a significant difference. The former contains a low quantity of fluorine ($\simeq 3\%$) while for the latter, the percentage is higher ($\simeq 20\%$.) For the coatings obtained at lower temperature (300°C) only a weak peak characteristic of fluorine ($F1s$ at 685 eV) is identified (6). The percentage is estimated lower than 1%, fluorine embedded in the film is associated neither with oxygen nor with carbon, which are not displayed on the spectrum presented in Fig. 4b, where the surface contamination has been taken off by ion bombardement. EDX analyses confirm the XPS results.

For molecule A the growth rate of the copper film with and without UV-ligth assistance is presented in Fig. 5 as the function of the reverse temperature (Arrhenius plot). For the same decomposition temperature, UV-ligth assistance improves the growth rate.

Fig. 3 - Surface morphology of coatings prepared from :
molecule (A) with UV irradiation : a : $T_s = 200^\circ\text{C}$, b : $T_s = 250^\circ\text{C}$, c : $T_s = 350^\circ\text{C}$
without UV irradiation : d : $T_s = 350^\circ\text{C}$
molecule (B) with UV : e : $T_s = 350^\circ\text{C}$
without UV : f : $T_s = 350^\circ\text{C}$

Fig. 4a - General XPS spectra of a coating obtained at 200°C by photo CVD from molecule (A) :
1. before Ar⁺ etching
2. after Ar⁺ etching

Fig. 4b - General XPS spectrum after etching of a coating obtained at 300°C by photo CVD from molecule (B)

The activation energies are different: 1,2 eV and 0,3 eV for the layers growing without and with UV-irradiation respectively. The improvement observed in the growth rate is a consequence of the UV-assistance.

Fig. 5 - Growth rate of photo-CVD and thermal CVD films produced from $\text{Cu}(\text{thd})_2$ versus substrate temperature.

X-Ray diffraction show that the films are crystalline. No orientations were displayed, all the intensity ratios I_{hkl}/I_{111} for the copper are near of those reported in the ASTM data for powder samples (fig. 6).

Fig. 6 - X-ray diffraction pattern of the film prepared from molecule (A) at $T_s = 250^\circ\text{C}$ by photo CVD.

4.-Conclusion :

From these preliminary experiments, various observation can be made. The use of UV-irradiation lowers the decomposition temperature. This point appears interesting for organometallic precursors.

In the case of Cu(hfa)_2 decomposition, the fluorine element is not present by UV-assistance decomposition while by thermal decomposition its amount is very high. The use of UV-irradiation seems to protect the organic part of the precursor and consequently no carbon and oxygen contamination is observed. Despite the low deposition temperature the coatings are crystalline.

Nevertheless, the surface morphology is granular and more experiments are necessary to improve it. Particularly, the experimental conditions must be changed to facilitate a best surface crystallization.

Concerning the mechanism of decomposition some questions arise. Particularly the reaction of decomposition with He as carrier gas is not satisfactory :

In effect the (L) ligands are ions and their evolution to neutral β -diketones needs the fixation of hydrogen atoms. Experiments under hydrogen gas or with a molecule which liberates a hydrogen atom would be useful to verify this point (3). The photochemical assistance facilitates the decomposition. The reactions in the homogeneous phase seem to be more important than in the case of thermal decomposition. In order to improve the knowledge of photo-assisted decomposition, various experiments under different experimental conditions are planned.

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