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Volatile Metals Coordination Compounds as Precursors for Functional Materials Synthesis by CVD-Method

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Abstract. The applications of such coordination compounds (chelates) as metal β -diketonates in different CVD techniques were examined. It was shown that high chemical and physical characteristics of these compounds allow their favourable use comparatively with other volatile compounds. The general rules in volatility and thermal stability of β -diketonates and their fluorine derivatives were discussed. The ways of preparation of various functional materials with specific properties were determined.

1. INTRODUCTION

Modern state of technology requires the development and perfection of existent techniques for metal oxides, carbides, nitrides protective coatings' production; synthesis of selective catalysts; production of functional materials for radio-, optical, acoustic electronics, powders with high degree of dispersion, ceramic whiskers, etc. Application of such high capacity, non environmentally pollutant, power and resources conservative technique as chemical vapor deposition allows to obtain new materials with given properties [1, 2].

Stable existence of reagents in vapor phase and feasible control of their decomposition on the heated substrate with solid precipitate and recycling gas products formation is necessary demand in all modifications of CVD technique. High volatility of precursors, that is high pressure of saturated vapors at the lowest temperatures is also desired.

Metal compounds able to evaporate and to condense without composition change at moderate temperatures (less than 700 - 800 K) are concerned as volatile thermally stable compounds. These compounds can be classified as:

- compounds with monodentant α -donor ligands (halides, aloxides, amides, α -metalorganic compounds);
- hydrides and borohydrides;
- coordination compounds with π -acceptor ligands (carbonyls, trifluorophosphines);
- organic π -complexes (cyclopentadienyl, arenes, allyls, etc.);
- salts of some organic acids (carboxylates, anhydrous nitrates, perchlorates);
- intracomplex compounds (chelates) (β -diketonates, their derivatives, dialkylditiocarbamates, tropolonates, etc.); and great amount of mixed ligand complexes simultaneously fall into different classes mentioned above. However only few metals in each of these classes could form compounds with required volatility and thermal stability.

To our mind intracomplex (chelate) compounds stable with almost all metals of periodic system are the most multipurpose.

Metals β -diketonates are the most typical and commonly used intracomplex compounds and can be successfully applied as precursors in various industrial modifications of CVD processes due to the complex of their following properties:

- rather high volatility at comparatively low temperatures (50-250° C);
- sufficiently low temperatures of thermal decomposition (150-550° C);
- formation of volatile gaseous co-products easily eliminated from reaction zone;
- water and oxygen resistance of a great number of complexes;
- air inflammability;
- low toxicity of complexes and the products of their thermal decomposition;
- comparatively low cost.

The possibility to change or to potentiate metal β -diketonates specific properties allowed us to develop various techniques for production of metal oxides used in microelectronics, high disperse metal and oxide powders; metal oxide and oxycarbide protective coatings.

2. VOLATILITY OF METAL COORDINATION COMPOUNDS

The high volatility of metal β -diketonates occurs because of their structural features. The high developed periphery of coordination compound's molecule shields its coordination junction by reducing both electrostatic (charge, dipole, etc.) and nonvalence (Van der Waals forces, hydrogen bonds, etc.) components of intramolecular interaction [3, 4].

The dependence of thermal stability for some metal β -diketonates and their adducts on temperature is shown in Fig. 1 [3, 4, 5].

Figure 1: The effect of metal and α -substituent nature on deposition temperatures of β -diketonates in vapor phase. (AA - 2,4-pentadione; TFA - 1,1,1-trifluorine-2,4-pentadione; HFA - 1,1,1,5,5,5-hexafluorine-2,4-pentadione; HFEN - 1,1,1,2,2,3,3-heptafluorine-7-ethyl-4,6-nonandione; HFH - 1,1,1,2,2,3,3-heptafluorine-4,6-heptanedione; DFH - 1,1,1,2,2,3,3,7,7,7-decafluorine-4,6-heptanedione).

It is evident that there is a general rule of volatility change depending on β -diketonate molecule structure. The volatility of coordination compounds with fluorine substituents is higher. In β -diketonates with straight chain of substituents the volatility lowers when the length of α -substituent increases.

From one hand adducts formation slightly lowers the volatility but on the other hand it considerably stabilizes the complex and expands the range of thermal stability. This fact becomes evident from the analysis of manganese (II) β -diketonates [6]. Anhydrous manganese (II) trifluorine- and hexafluorine-2,4-pentadionates are unstable and easily decompose at temperatures of 100-110°C with partial sublimation (20-30%). When a donor molecule (e.g. dimethyl formamide or tributylphosphine oxide) is introduced into β -diketonate molecule thermal stability of the complex increases - the decomposition begins at 220-240°C and sublimation occurs at 100° and 130°C respectively.

Thus the volatility of β -diketonate complexes occurs mainly because of high shielding of coordination junction by atoms of ligand substituents. Ligand substituents form molecular periphery with weak atom-atom activity that considerably lowers the average value of intermolecular interaction. From another point of view β -diketonates thermal stability in vapor phase depends on structural features of coordination compounds. The above considered compounds are intracomplex compounds where metal atom is enclosed into three interconnected shells: coordination junction, skeleton ligand groups and periphery shell formed mainly by substituents.

In the case of condensed state the temperature rise causes the periphery excitation, torsion rotation and oscillations of ending groups in substituents amplification and intramolecular upward transition of central atom through the ligand chain. Torsion rotation and oscillations of ending groups decrease intermolecular potential due to higher shielding level and intermolecular movements of central atom increase the value of potential energy of molecule without its structural disturbance. Thus gas phase transition of molecules becomes possible due to intramolecular bonds splitting.

In the case of gas phase the temperature rise increases probability of intermolecular collisions and the energy of molecules. Electron density delocalization in the coordination junction and in the skeleton of complex causes redistribution of entering energy through atoms and bonds.

Average temperatures of metal β -diketonates decomposition in vapor phase

Table 1

Precursor	Decomposition atmosphere	Decomposition product	Average decomposition temperature	Precursor	Decomposition atmosphere	Decomposition product	Average decomposition temperature
Cu(AA) ₂	N ₂ , N ₂ H ₄	Cu(met.)	380	In(AA) ₃	Ar, O ₂	In ₂ O ₃	400
Cu(TFA) ₂	"	"	285	In(HFA) ₃	"	"	230
Cu(HFA) ₂	"	"	195	Zn(AA) ₂	O ₂	ZrO	420
Cu(HFEN) ₂	"	"	255	V(TFA) ₃	"	V ₂ O ₅	335
Cu(HFH) ₂	"	"	240	VO(AA) ₂	"	VO ₂	400
Cu(DFH) ₂	"	"	165	Cr(TFA) ₃	"	Cr ₂ O ₃	315
Co(AA) ₃	H ₂	Co(met.)	420	Mn(TFA) ₂	"	MnO ₂	185
Ni(AA) ₂ ·2D	"	Ni(met.)	420	Fe(AA) ₃	"	Fe ₂ O ₃	440
Rh(HFA) ₃	"	Rh(met.)	250	Fe(TFA) ₃	"	"	250
Ir(AA) ₃	"	Ir(met.)	400	Co(TFA) ₃	"	Co ₂ O ₃	270
Be(AA) ₂	Ar, O ₂	BeO	480	Ti(HFA) ₄	O ₂ , 10torr	TiO ₂	490
Al(AA) ₃	"	Al ₂ O ₃	520	TiO(TFA) ₂	O ₂	"	500
Al(TFA) ₃	"	"	430	Zr(AA) ₄	O ₂ , 10torr	ZrO ₂	525
Al(HFA) ₃	"	"	310	Zr(HFA) ₄	"	"	500
Al(DPM) ₃	"	"	565	Hf(AA) ₄	"	HfO ₂	550
Ga(AA) ₃	"	Ga ₂ O ₃	440	Hf(HFA) ₄	"	"	600

This buffering process has a certain capacity and determines thermal stability region of coordination compounds in vapor phase (table 1 and fig. 1).

3. MECHANISM OF THERMAL DECOMPOSITION

As a rule thermal decomposition of coordination compounds and particularly metal β -diketonates could be considered as homolytic dissociation of bonds. As a result of bond destruction in ligand skeleton and li-

and thermal fragmentation such neutral particles as the metal and radicals or molecules of oxygen and carbon containing metal fragments are formed.

Considering the probability of sequential fragmentation these processes could be written as following schemes:

Since electron density in metal β -diketonate is delocalized both processes of homolitical dissociation and of complex elimination may occur with equal probability.

The following possible ways of metal β -diketonates thermal dissociation may be considered:

1. Ligand splitting
2. Oxygen elimination I
3. Oxygen elimination II
4. Carbonoxide elimination I
5. Carbonoxide elimination II
6. Carbonoxide elimination III
7. Elimination with α -groups
8. Hydride (fluoride) elimination.

The results of mass-spectroscopy and thermal analysis of decomposition of metal β -diketonates [7,8] showed that occurring of specific fragmentation way depended on central atom's nature, nature of ligand or of substituent in case of β -diketone and type of atoms formed coordination junction ($-O,O-$; $-O,N-$; $-O,S-$; etc.) as well as on conditions of thermal decomposition: temperature, pressure, oxidizing or reducing atmosphere during pyrolysis process presence of deactivated additives, surface catalysis and some other factors.

When atomic number of metal within the limits of subgroup increases the probability of pure metal precipitation during metal β -diketonate fragmentation rises.

Recently the application of thermal decomposition processes of metalorganic compounds (MOC) for deposition of coatings has widened out significantly. The possibility to change purposefully the properties of coordination compounds during their synthesis allows them to be successfully applied for production of various materials using CVD technique.

4. METAL FILMS

Unfortunately the deposition of pure metal films using metal β -diketonates or their N-analogs is available only for some elements: metals of platinum group (Pd, Pt, Ir, Rh) and gold; copper and metals of VII group (Ni, Co, Fe) [9].

Processes of vapor phase decomposition were carried out either under initial vacuum or in gas-carrier flow when β -diketonates evaporation temperature range and their decomposition temperature range were 170-250°C and 300-450°C respectively. When fluorine β -diketonates and H_2 as gas carrier were used the sublimation and decomposition temperatures reduced down to 80-150°C and 250°C correspondingly and deposition rate increased.

The main disadvantageous of these techniques are partial contaminant of metal films by oxides and carbides, a need for hydrogen using at rather high temperatures, low films growth rate.

The results of our investigations showed that adducts formation raised covalence of the bond metal- β -diketone and hence metal phase precipitated as a result of the reaction of thermal decomposition. Besides the reducing of metal accounts for electron transfer from organic base but not from β -diketonate fragment and the last one does not take part in oxidizing-reducing processes and is less destruction-prone. Parameters of pure metal films deposition using adducts of trifluoro- and hexafluoroacetylacetonates with ethylene glycol (EG), monoethanoleamin (MEA) and diethylamine (DEA) are given in table 2.

Table 2

Optimal conditions of Cu, Ni, Co metal films deposition

Cophounds	Temperature of evaporator, °C	Substrate temperature, °C	System pressure, Torr	Deposition rate, $\mu\text{m}/\text{min}$
Cu(HFA) ₂ :2MEA	90	300	8-12	0.05
Cu(TFA) ₂ :2DEA	80	270	5-10	0.03
Cu(HFA) ₂ :2EG	135	280	5-10	0.06
Cu(TFA) ₂ :2MEA	125	320	5-10	0.10
Co(HFA) ₂ :2EG	100	300	8-12	0.05
Co(HFA) ₂ :2MEA	100	250	5-10	0.03
Ni(HFA) ₂ :2MEA	130	280	5-10	0.03
Ni(TFA) ₂ :2MEA	135	320	5-10	0.02

The deposited films are free from oxide and carbide phases, have high adhesion to ceramics, glass ceramics, metals, including even titanium and tungsten solid alloys.

5. OXIDE FILMS

Since thermal decomposition of the most of elements occurs by the way of oxygen elimination (schemes II, III) the formation of oxide phases in oxidizing atmosphere under CVD-processes is possible for almost all elements that form volatile thermally stable coordination compounds with β -diketones.

High quality oxide films of Be, Al, In, Ga, Zn, Ti, Zr, Hf, Th, Ta, Fe, and others were successfully deposited using CVD techniques [10]. For instance the preparation of zinc oxide, aluminum oxide, HTSC films with high characteristics were discussed in the papers published in this issue.

6. CONCLUSIONS.

High volatility, thermal stability, air hydrolysis resistance, non toxicity and explosion proofness, rather simple synthesis of various metal coordination compounds and therefore their low cost are the main characteristics of β -diketonates used as precursors in CVD techniques.

We consider the application of β -diketonates to be alternative to such volatile compounds as alkyls, carbonyls, halides normally used for production of different functional materials.

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