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Preparation of thin copper films from the vapour phase of volatile copper(I) and copper(II) derivatives by the CVD method

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Abstract. The main chemical aspects of the preparation of thin copper films from the vapour of monovalent and divalent copper derivatives as precursors in the CVD technique are considered. Data on the methods of synthesis and the properties of various types of these compounds are generalised and described systematically. The possible decomposition mechanisms of copper compounds under CVD conditions are discussed. The prospects of using the CVD technology for the preparation of thin copper films in integrated circuits of microelectronic devices are outlined. The bibliography includes 432 references.

I. Introduction

Micro- and nanoelectronics are the most promising fields for the application of thin copper films. Such films are used as conducting paths in large-scale and very-large-scale integrated circuits (LIC and VLIC, respectively); they make an alternative to aluminium films. It is known that non-doped aluminium films used as electric wiring in LIC and VLIC have a number of drawbacks. First, discontinuity of aluminium films is observed during operation of integrated circuits because of the large atom electromigration coefficient, which was shown by calculations to be due to relaxation of the bulk upon passage of a flow of vacancies.[1] On the other hand, the electromigration coefficients in the layers of copper atoms are a few orders of magnitude smaller than in aluminium atom layers. Second, the specific electric resistance (SER) of copper is 30% smaller than that of aluminium. The addition of copper or silicon (2 at.% – 4 at.%) to aluminium films does not eliminate all the drawbacks of aluminium as a material for interconnections in LIC and VLIC.[2–9]

In addition, thin copper films are used in devices which employ the effect of the gross magnetic resistance in polycrystalline Co/Cu multilayers. The thickness of the cobalt and copper layers ranges from a few fractions of a nanometre to several nanometres.[10–14]

Copper films are deposited onto substrates. Silicon and silicon dioxide are the most common substrate materials. The diffusion coefficients of copper into silicon and silicon dioxide are high, they are a few orders of magnitude higher than those of other metals. The use of barrier layers in order to decrease this coefficient was suggested. At first, it was attempted to solve this problem by means of PVD (Physical Vapour Deposition) technology, using such methods as thermal evaporation, plasma spraying, magnetron or laser scattering, as well as by spray deposition of thin layers of other metals (Cr, Co, W, Ti, Ta) on an SiO_2 surface. However, little progress has been made in this direction. Later, metal nitrides used as the barrier layer materials showed better performance than the pure metals.

The common drawback of PVD technology is the necessity of heating a substance to high temperatures (above the vaporisation temperature). Therefore, intense development of CVD (Chemical Vapour Deposition) technology has started in recent years; this technique involves chemical methods of deposition of thin films from the gas phase using metal-containing compounds. Chemical methods have a number of advantages over physical methods. These include relatively mild conditions for film deposition, comparatively low vaporisation temperatures of the starting compounds, conditions favourable for good adhesion of the films to the substrate, wider technological prospects for the development of microelectronic devices with required parameters.

This review considers the chemical methods used in CVD technology for the preparation of copper films from volatile copper(II) and copper(I) derivatives. The main attention is given to work published within the period from 1991 to 1999, although earlier fundamental studies have also been taken into account.

The majority of compounds which we name 'copper-containing compounds' (CCC) correspond to copper complexes with copper – oxygen bonds. As to the specific CCC types, the review mentions virtually all classes of compounds considered as promising starting compounds for CVD technology. Many of these compounds have not yet found application in the synthesis of copper films. Nevertheless, we felt it worthwhile to mention them as well, at least because it is quite possible that other CCC of the same classes may be suitable for CVD processes.

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II. Equipment used in CVD processes

A vast literature (see, *e.g.*, Refs 15–28) is devoted to CVD technology. In essence, the CVD process involves evaporation of volatile metal-containing compounds followed by transfer of their vapour to a reaction compartment, where the starting compound is decomposed and the decomposition products are deposited onto a substrate in the form of a film. Most commonly, decomposition is accomplished by means of thermolysis, sometimes along with exposure to plasma or irradiation. Side products are removed from the reaction zone in the form of vapour.

If the process is carried out with the use of an inert gas as the carrier for the vapour of the starting compound, it is usually purified from oxygen and other admixtures by passing it preliminarily through adsorbents or a membrane. Hydrogen is purified by passing it through palladium.[29] Liquid compounds are injected using devices based on controlling the mass consumption rate.[30, 31]

Various designs of reactors have been developed for the CVD processes.† As an example, Fig. 1 shows a simple reactor scheme for pyrolytic deposition of films by evaporation of metal-containing compounds followed by transportation of the vapour to the deposition zone.

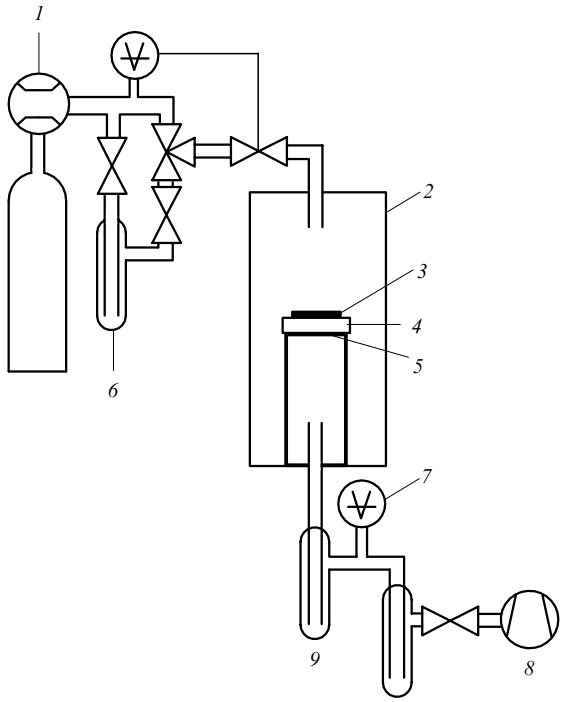


Figure 1. The simplest CVD reactor scheme;[40]
(*1*) flow controller, (*2*) reactor, (*3*) substrate, (*4*) heater, (*5*) thermocouple, (*6*) CCC source, (*7*) manometer, (*8*) pump, (*9*) liquid nitrogen trap.

Many reactor designs and film deposition processes have been patented.[35, 41–44] A number of firms manufacture serial reactors, *e.g.*, MR-200 (Cambridge Instruments, Great Britain),[45] EMCORE (GS/3300 firm, USA) with a rotating disk and uniformity of the substrate temperature to within 1 °C,[46] EPISON (Thomas Swan Ltd, Great Britain).[47, 48]

† They can arbitrarily be divided in two groups: vertical[32–35] and horizontal.[35–39] A review of the equipment used before 1972 for the deposition of films and coatings by CVD can be found in Ref. 15 (see p. 180 *ff*).

High-performance technological equipment for the preparation of thin layers by CVD has been developed at the Samsung company's institute (Republic of Korea). This equipment makes it possible to manufacture more than 10 000 devices (diodes, photo diodes, *etc.*) simultaneously.[36]

The design of a CVD reactor in which hydrogen plasma is used was reported.[49] High-quality copper films with a SER of 2.0 μΩ cm are obtained in such reactors.

In recent years, combined instruments (of the so-called cluster type) for the deposition of any type of thin films by physical or chemical methods, including CVD technology, have appeared (see, *e.g.*, Ref. 50). These instruments allow one to deposit multilayer coatings from different materials.[51] An example of such an instrument is shown in Fig. 2.

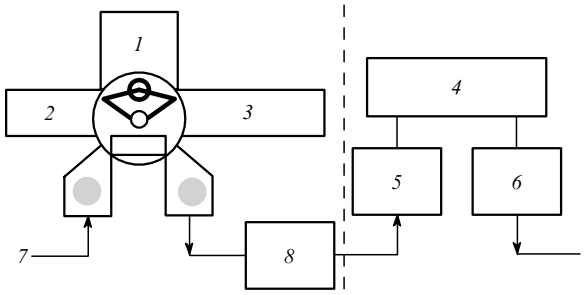


Figure 2. Block diagram of a 'cluster' apparatus for the preparation of thin films;[52]
(*1*, *2*) process modules, (*3*) observation module, (*4*) multifunctional module (exposure, polishing, *etc.*), (*5*) sample preparation module, (*6*, *8*) measuring modules, (*7*) support inlet.

CVD methods are successfully used if high-quality and uniform films (both with respect to the composition and thickness) of large area are required. For this purpose, the substrates in the reactor are rotated; laminar gas streams in the reactor and uniform heating are provided. In this way, thickness uniformity within 2% and chemical composition uniformity within 1% can be achieved over the entire film surface.[53–56] Visualisation of convective flows in the growth chamber can be provided by laser illumination of dispersed particles or by creation of a 3D image by interference holography.

The production of integrated circuits requires the preparation of planar deposited copper layers. For this purpose, the technology of chemical and mechanical polishing of copper films has been developed which includes treatment of the film surface with a suspension of fine SiO_2 and Al_2O_3 particles; benzotriazole is added as an oxidant if necessary. In the latter case, the rate of film surface polishing depends on the concentration of benzotriazole.[57, 58]

The waste gases are utilised using catalytic combustion, physical adsorption with activated carbon with or without oxidation and dry purification in reaction columns.[59, 60] The CS-GmbH company (Germany) has developed three types of gas absorbents: absorbing cartridges (Cleanvent), washing and purifying systems (Cleansorb) and emergency absorption systems (Clean-Protect). The Cleanvent cartridges are intended for *in situ* removal of hazardous gases from gas distribution systems.[61]

III. Barrier layers preventing the diffusion of copper atoms into the substrate

Diffusion of copper atoms into the substrate during the operation of microelectronic devices impairs their characteristics. This can be prevented by means of barrier layers between the copper film and the substrate. These layers consist of certain metals and/or binary compounds and can be obtained using PVD or CVD

technologies. CVD favours the formation of amorphous films, as shown, *e.g.*, for tantalum nitride.[62]

1. Barrier layers prepared by PVD methods

Originally, diffusion of copper atoms into silicon as the most common substrate was prevented by thin barrier layers of diamond-like carbon and metal films obtained by PVD methods.[63, 64] Films of various binary compounds, primarily titanium, tungsten and tantalum silicides, borides and nitrides, are also suitable for this purpose.[65–85]

Tungsten and tantalum are regarded as the best metals for the deposition of barrier layers by PVD, as they have the smallest self-diffusion coefficients in the series Ti > Cr > Nb > Mo > Ta ~ W.[64] After deposition, the layers are exposed to annealing in hydrogen for 1 h at 600 °C.[64]

Metal film barrier layers were gradually replaced by films of titanium and tungsten silicides and nitrides.[65–74] In this case, the thermal stabilities of the layers increased to 500 °C (WSi_x multilayer)[68] and 700 °C ($WSiN/WSi_x/W$ multilayer).[69] The layers of solid solutions of titanium in tungsten, TiW (30 at.% Ti), have somewhat different characteristics. If the barrier layers are 100 nm thick, the Cu/TiW/Si multilayers are stable up to 775 °C, and their stabilities increase to 850 °C upon keeping in air. In the latter case, 0.2 at.% of oxygen was detected in the film.[72]

The pure tantalum film 10 nm thick is an efficient barrier against the diffusion of copper into the silicon substrate up to 500 °C.[69] The films of tantalum nitrides, *viz.*, Ta_2N, TaN, and those of the $Ta_{36}Si_{44}N_{50}$ alloy provide even more reliable protection against penetration of copper atoms into the silicon substrate.[75–77, 79, 82] The characteristics of barrier layers are listed in Table 1.

2. Barrier layers prepared by the CVD method

The compositions and properties of barrier layers obtained by thermolysis using the CVD technology depend both on the conditions of the process and on the properties of the starting volatile compounds.

Generally, the CVD method allows one to work with a wide range of starting volatile compounds of metals (for example, 15 starting volatile compounds have been listed [78] for the preparation of just one compound, TiN); layers with required properties can be obtained by varying the process parameters (vapour phase composition, deposition temperature, pressure).

Table 2 lists the starting compounds and some characteristics of CVD processes for the preparation of thin barrier layers of TiN, TaN, Ta, Ti, Cr, and Co.

It should be noted that PVD methods for the preparation of thin layers from the gas phase (spraying of compounds by bombardment with high-energy electrons and ions, magnetron and radio-frequency spray deposition, *etc.*) require that higher energy was applied to the substance for evaporation. The growth of films generally starts with the formation of separate islets-droplets, which subsequently merge to form a continuous film. Polycrystalline films are mostly formed; this is undesirable in terms of the diffusion of copper atoms, as the grain boundaries have higher diffusion coefficients than the grain bulk.

On the other hand, CVD of compounds from the gas phase generally occurs at lower temperatures. In this case, amorphous films are formed. The diffusion coefficients of copper atoms through the bulk of such films are smaller than through the grain boundaries. This is one of the advantages of chemical methods for film deposition from the gas phase over physical methods.

Yet another advantage of CVD methods is the possibility of selective processes, *i.e.*, preferential deposition, in particular of copper, on one substrate material or surface area with certain mechanical characteristics with respect to another material or surface area. This is a very useful feature for the production of microelectronic devices, as it can replace lithographic template preparation in the creation of an integrated circuit.

Table 1. Parameters of barrier multilayers preventing the diffusion of copper atoms into the silicon substrate.

Multilayers	Deposition method	l /nm	T_1 /°C	T_2 /°C	Ref.
Cu/(DLC)/Si	PECVD	100	400	–	63
Cu/M/Si, M = Cr, Ti, Nb, Mo, Ta, W	CVD	60	600	–	64
Cu/Cr/Si	"	10–40	400	500	65
Cr/Cu/Co/Au	"	320	400	500	66
Cu/CrN_x/Si	"	50	70	800	67
Cu/Cr/Si	"	50	500	–	67
Cu/WSi_x/Si	PACVD	50	500	550	68
$Cu/WSiN/WSi_x/W$/Si	"	450	650	650	69
$Cu/WSiN/WSi_x$/Si	"	50	500	650	70
Cu/TiB_2/Si	LPCVD	150	650	–	71
Cu/TiW/Si	PECVD	100	775	850	72
$Cu/TiW/Al/SiO_2$/Si	PVD	50/100	450/500	–	73
Cu/TiN/Si	LPCVD	40	450	–	74
Cu/TiN/Si	CVD	50	550	–	83
Cu/TaN/Si	PVD	180	500	950	75
Cu/TaN/Si	"	–	–	800	78
$Cu/TaN/SiO_2$/Si	"	25/10	700/600	800	81
Cu/Ta_2N/Si	"	50	550	700	77
Cu/Ta/Si	"	20	320–630	630	80
$Cu/Ta + CeO_2$/Si	"	–	800	–	84, 85

Note. The following designations are used: l is barrier layer thickness; T_1 is the upper limit of the stability temperature range; T_2 is the annealing temperature where new phases are formed; DLC is diamond-like carbon; PACVD is plasma-activated CVD method; LP is low pressure.

Table 2. Process parameters for CVD deposition of TiN, TaN, Ti, Ta, Cr and Co barrier layers.

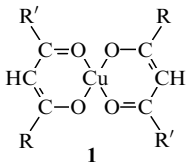
Starting compound	T /°C	T_g /°C	Carrier gas	P /Torr	Substrate	Ref.
$Ti(NMe_2)_4$	–	100 – 500	NH_3	1 – 20	Si	86, 87
	45	350 [a]	He, N_2, Ar	1	SiO_2/Si	88
	60	200 – 450	Ar	0.8 – 5	SiO_2/Si	89
	–	300 – 580	NH_3	–	–	84
	–	377	NH_3	–	$TiSi_2$, Al, Cu	90
	–	300 – 350	NH_3	2 – 7.5	InP	75
	–	250 – 500 [a]	N_2, H_2, NH_3	0.5 – 5	Si	87, 91
	–	425	Ar, NH_3	10	Si	92
	–	300 – 580	NH_3	–	Si	93
$Ti(NEt_2)_4$	40 – 50	425	NH_3	10	Si	92
$(Bu^t_2N)Ta(NEt_2)_3$	–	450 – 650	N_2	0.2	Si	94
$CpTi(C_7H_7)$	–	300 – 600 [a]	H_2, N_2, NH_3	–	Si	95
$(Cp)_2Ti(N_3)_2$	–	350 [b]	N_2	–	Si	96
$Ti(OPr^i)_4$	–	500 – 550	N_2, H_2	–	steel	97
$Ta(NEt_2)_5$	285	350 – 400	–	–	–	98
Ar_2CrI	80 – 82	320	–	–	–	99
$(C_6H_5COOEt)_2Cr$	25 – 35	260	–	–	–	100
$Co_2(CO)_8$	–	200 – 300	H_2	0.01 – 0.1	SiO_2, Si	101, 102
$CpCoEt_2$	–	240 – 400	H_2	–	SiO_2, Cu, Al	103
$Co(acac)_2$	–	320 – 350	–	–	glass	104
$Co(acac)_3$	–	320 – 350	–	–	"	104
$Co(CO)_3NO$	–	350 – 480	Ar, H_2	1.5	SiO_2/Si	105

Note. The following designations are used: T is the vaporisation temperature of the compound; T_g is carrier gas temperature; P is pressure in the reactor.
[a] In plasma. [b] Under UV irradiation.

IV. The starting copper-containing compounds: copper(II) derivatives

Volatile copper(II)-containing compounds had been synthesised long before the CVD technology appeared. Of these, chelate complexes of copper(II) with β-diketones **1** have been studied most thoroughly.

Copper(II) acetylacetonate, $Cu(acac)_2$ (**1**, R = R′ = Me) synthesised in the past century,[106] was the first compound of this series which may be regarded as an appropriate volatile CCC for CVD. By the early 1960s, the number of copper(II) β-diketonates with various starting β-diketones exceeded sixty.[107 – 109]



1

Initially, the application of these compounds was limited to their use as convenient labels for characterisation of the corresponding β-diketones and in gas chromatography for the separation of metals.[109] As a matter of fact, the use of copper β-diketonates in CVD technologies began in 1965 when the first study devoted to the CVD synthesis of thin copper films based on β-diketonates appeared.[110] To date, there are several reviews dealing with copper β-diketonates as volatile CCC (see, for example, Refs 26 and 111), but they did not cover the work published in recent years.

Certainly, not all copper(II) β-diketonates and their derivatives are suitable for CVD processes. The synthetic accessibility of the starting β-diketone is of certain importance, but the practical value of a particular copper(II) β-diketonate is determined by the combination of its physicochemical properties.

The relationship between the volatilities of metal β-diketonates (including that of copper) and their structures was analysed by Mazurenko *et al.*[112, 113] (see also the review by Tsyganova and Dyagileva [114]). The main criteria of stability of these compounds in the vapour phase have been stated in these reports. It is believed [113] that the rather high volatilities of these compounds are due to shielding of the coordination unit by the highly developed 'periphery' of the molecules, which decreases the contributions of the electrostatic and intermolecular interactions to the intermolecular potential.

However, volatility is a necessary but insufficient condition for the applicability of compounds in CVD technology. The basic requirements to the starting CCC are as follows:[113] the ability to undergo sublimation in low vacuum at as low temperatures as possible, providing as high a vapour pressure as possible; the ability to undergo sublimation and resublimation without decomposition; the ability to undergo thermolytic decomposition on a substrate surface at as low a substrate temperature as possible with a minimum possible content of admixtures in the resulting copper film.

Analysis of these requirements makes it possible to conclude that the thermolytic stability of the starting compound should have an optimum. In the best case, an insufficiently stable compound will reach the substrate surface as decomposition products, which is unfavourable for reproducibility of the process. If the compound is very stable, high substrate temperature (or additional energy in the form of radiation) is inevitably required for thermolysis, which generally affects adversely the film quality.

The starting volatile copper(II) derivatives with optimum technological properties for the CVD method have been sought among several basic groups of compounds considered below.

1. Copper(II) β-diketonates with alkyl groups

The main advantage of copper(II) β-diketonates with alkyl groups is their synthetic accessibility. However, they were not the first compounds used for the development of the CVD preparation of copper films; their polyfluorinated analogues were the first substances.[110, 115, 116] This is most probably due to the rather low volatilities of this type of copper(II) β-diketonates.[117] The β-diketones required for the preparation of metal β-diketonates can be synthesised rather easily by the Claisen condensation of the corresponding ketones with esters in the presence of nucleophilic reagents.[118]

$$RCOOEt + CH_3COR' \xrightarrow[-EtOH]{EtONa} RCOCH_2COR'$$

The suitability of copper(II) acetylacetonate $Cu(acac)_2$ and copper(II) dipivaloylmethanate $Cu(DPM)_2$ in CVD processes was considered. The latter compound is more volatile than $Cu(acac)_2$ because the β-diketone has a branched hydrocarbon chain (see **1**, $R = R' = Bu^t$).[116]

Substituted copper(II) acetoacetates[117] (Section IV.4a) provide an alternative to these compounds in the hydrocarbon series.

a. Synthesis and physicochemical properties

The main method for the synthesis of $Cu(acac)_2$ and other copper(II) β-diketonates with alkyl groups involves the reaction of the corresponding β-diketone or its hydrate with a hot aqueous solution of copper(II) acetate[119] or a mixture of a water-soluble copper(II) salt with sodium acetate.[120] Copper β-diketonate hydrates are usually obtained in this way; anhydrous compounds are obtained by heating or by keeping the hydrates over H_2SO_4.[120] It was noted, however, that the formation of a hydrate is untypical of $Cu(acac)_2$.[121]

Direct reaction of copper(II) acetate with an anhydrous β-diketone, which occurs in several minutes in boiling β-diketone, is also possible.[119]

$$Cu(Ac)_2 + 2RCOCH_2OR' \xrightarrow[-2H(Ac)]{} Cu(RCOCH_2COR')_2$$

The structure and spectral properties of the simplest β-diketonate, *viz*., $Cu(acac)_2$, have been studied rather thoroughly: all bond lengths and bond angles in the $Cu(acac)_2$ molecule have been determined;[122] quantum-chemical calculations of the electronic structure of $Cu(acac)_2$ have been carried out;[123,124] the ESR spectra of this compound have been recorded (see, *e.g*., Refs 125 and 126); a detailed assignment of its IR spectral bands has been performed.[127]

When deciding whether a compound can be used in CVD, its molecular structure and thermogravimetric data are of special importance. It was shown that in $Cu(acac)_2$ and other copper(II) β-diketonates, the separate molecules form infinite chains through intermolecular copper–chelate ring carbon bonds[128,129] with a bond length of 0.301–0.312 nm. This interaction complements the coordination of copper atoms to give a strongly stretched tetragonal bipyramid. The relative instabilities of these intermolecular bonds can be a reason for the volatility of this class of compound.[113]

The thermodynamic parameters of the $Cu(acac)_2$ molecule are listed in Ref. 130. The vapour pressures of this compound were measured at various temperatures (for example, it is ~0.3 Torr at 150 °C) and the temperature dependence of the vapour pressure was obtained.[131] It was shown by thermogravimetry that $Cu(acac)_2$ is sublimed completely and does not undergo decomposition in an inert atmosphere.[132] On the other hand, the results of thermogravimetric analysis of $Cu(acac)_2$ in air suggest that a single-step thermal decomposition occurs at 305°C.[133] The usual temperature range of $Cu(acac)_2$ sublimation in a CVD process is 100–170 °C.[134]

Dipivaloylmethane H(DPM) and $Cu(DPM)_2$ were first obtained by condensation of ketones with esters in the presence of $NaNH_2$.[121] Simpler methods for the synthesis of $Cu(DPM)_2$, *e.g*., the reaction of H(DPM) with an aqueous solution of $CuSO_4$ in the presence of sodium acetate, were developed later.[135] The properties of $Cu(DPM)_2$ have also been studied rather thoroughly: the crystal structure has been determined;[136] thermogravimetric data have been obtained showing that in a nitrogen atmosphere $Cu(DPM)_2$ sublimes completely at 240–245 °C;[131,132] its sublimation enthalpy (74.8 kJ mol^{-1}) and entropy (132.2 J mol^{-1} K^{-1}) have been determined.[135] Analysis of thermogravimetric curves for a wide range of copper(II) β-diketonates with alkyl groups[131,132] showed that $Cu(DPM)_2$ is actually the most volatile compound in the series where both ligands are identical (the compounds with different ligands are less accessible synthetically).

b. The mechanisms of decomposition of copper-containing compounds on substrate surfaces

The mechanisms of formation of copper films from copper(II) β-diketonates with alkyl groups in CVD processes have been studied in various respects. A number of studies (see, *e.g*., Refs 137, 138 and references cited therein) deal mainly with the physical aspects of the growth of copper films and its mathematical simulation.

Turgambayeva *et al*.[139,140] used mass-spectrometric data to analyse the thermolysis of $Cu(acac)_2$ molecules in the vapour phase in a vacuum as well as in a stream of oxygen and hydrogen. It was shown that, depending on the temperature, thermolysis can result in various volatile organic products, such as H(acac), acetone, ethyl methyl ketone, *etc*. The kinetic and activation parameters of the thermal decomposition of $Cu(acac)_2$ in the vapour phase were reported;[140,141] this process was described satisfactorily by a first-order kinetic equation. It was concluded on the basis of IR spectra of $Cu(acac)_2$ that the decomposition starts with destabilisation of the coordination unit at the copper–oxygen bonds of the complex.[142] A similar study of the kinetics and thermal decomposition products in the vapour phase was also carried out for $Cu(DPM)_2$.[143]

It is very important to have data on the mechanism of thermolytic decomposition of compounds directly on the substrate in order to bring the CVD processes to perfection.

One of the first schemes suggested for the description of $Cu(acac)_2$ decomposition on heated substrate surfaces involved a radical mechanism:[16]

$$Cu(acac)_2 \longrightarrow (acac)Cu^{\bullet} + (acac)^{\bullet},$$

$$(acac)Cu^{\bullet} \longrightarrow Cu + (acac)^{\bullet}.$$

It is considered that subsequent decomposition of the acetylacetone radical will produce contaminants (admixtures of carbon and copper oxides) in the film.

A somewhat different scheme of $Cu(DPM)_2$ decomposition is described in Refs 144–146. A study of the thermolysis mechanism by *in situ* Fourier IR spectroscopy at a substrate temperature of 500 °C and a pressure of 20 Torr showed that the process starts with the cleavage of the C–C bonds of the chelate ring accompanied by simultaneous partial elimination of the *tert*-butyl groups. As a result, isobutene is formed. The thermolysis is abruptly accelerated at 600–700 °C; the films formed at temperatures above 600 °C are considerably contaminated with carbon. The overall decomposition equation is:

$$Cu[(CH_3)_3COCH_2OC(CH_3)_3] \xrightarrow{T} Cu + 2C + 4CO\uparrow + 4H_2C{=}C(CH_3)_2\uparrow + 3H_2\uparrow.$$

The interaction of $Cu(DPM)_2$ with a substrate surface was studied by IR spectroscopy during the decomposition of the vapour in the presence of H_2O on the (100) planes of SiO_2 crystals (see Refs 147 and 148) and $SrTiO_3$ crystals (see Ref. 149) with formation of a copper film.

It was shown that the film formation on the SiO_2 surface starts with stoichiometric chemisorption of the copper(II) β-diketonate involving reactive surface OH groups. This reaction occurs even at 50 °C and results in the disappearance of the peak assigned to OH groups in the IR spectrum.[148] It was found that one $Cu(DPM)_2$ molecule at the surface is coordinated with two or three OH groups.

In the presence of water vapour providing adsorbed water on the substrate or upon direct participation of OH group protons, decomposition of $Cu(DPM)_2$ with elimination of one H(DPM) molecule and formation of copper(I) dipivaloylmethanate Cu(DPM) occur, as confirmed by XPS data.

$$Cu(DPM)_{2\,(ads)} + H_2O_{(ads)} \longrightarrow H(DPM)\uparrow + OH^-_{(ads)} + Cu(DPM)_{(ads)}$$

As shown in more detail for polyfluorinated analogues (see Section IV.2.b), the intermediate copper(I) compound can undergo both reduction and disproportionation to give metallic copper and the original copper(II) compound.

This reaction on the SiO_2 surface also gives copper(I) oxide.[147]

Deposition of copper onto the $SrTiO_3$ substrate was preceded by bombardment with Ar^+ ions giving Ti^{3+} ions in the near-surface layer, which favoured the adsorption of the H_2O molecules. The mechanism of $Cu(DPM)_2$ transformations on the $SrTiO_3$ substrate is similar to that described above for the SiO_2 substrate.[149]

Improvement of copper film characteristics in the CVD process based on copper(II) β-diketonates with alkyl groups, in particular a decrease in the SER, is reached under additional UV irradiation. Zama *et al.*[150] believe that in this case, UV irradiation favours the migration of the copper atoms over the growing copper film surface, thus decreasing the grain size and, hence, producing a smoother surface.

c. Preparation and characteristics of copper films

The use of copper(II) acetylacetonate as the starting CCC for the preparation of thin copper films by CVD began in the early 1990s,[134, 151] though some earlier works on this process (mostly patents) are known (see Ref. 16).

A study of CVD of copper films from $Cu(acac)_2$ vapour onto a SiO_2/Si substrate at 220–250 °C (with an argon–hydrogen mixture as the carrier gas) showed that the structure and morphology of copper films are primarily determined by two factors, *viz.*, the deposition rate and the partial pressure of hydrogen in the carrier gas.[151] In a later study,[152] polycrystalline copper films were obtained from $Cu(acac)_2$ vapour in pure hydrogen. The preparation of copper films with satisfactory characteristics from the same CCC but at higher substrate temperatures (T_s) of 300–450 °C (Table 3) has been patented.[153]

A high temperature is required for CVD with $Cu(acac)_2$ as the starting compound. It was suggested that it may be decreased (by ~ 75 °) and the film deposition rate increased by using UV irradiation.[154]

Yet another way for the activation of the CVD process involves the plasma-activated decomposition of $Cu(acac)_2$ vapour in hydrogen (PACVD), which allows generation of reactive hydrogen species at rather low temperatures.[155] For example, smooth thin copper films with a low SER (see Table 3) were obtained from $Cu(acac)_2$ vapour.[134] The decomposition was carried out in the presence of hydrogen (carrier gas) up to a substrate temperature of 300 °C; it was found that at higher temperatures decomposition does not depend on the nature of the carrier gas. This is apparently due to the fact that the amount of hydrogen formed upon intense pyrolysis in this temperature range is sufficient for the reduction of copper.[146] However, the presence of even small concentrations of O_2 results in an abrupt increase in the SER of the films.

If $Cu(DPM)_2$ vapour is used, the copper film growth on a quartz substrate starts at 350 °C.[133, 156] The polycrystalline films obtained by this method [133] were preferentially oriented along the [111] direction and had a thickness > 300 nm and an SER of 10 μΩ cm (see Table 3). According to XPS data, carbon and oxygen were the main admixtures in this case (their total content was up to 10%); their simultaneous presence in the film could result from the reaction of copper with CO formed upon decomposition.[146]

The specific electric resistance of copper films obtained [116] from $Cu(DPM)_2$ vapour increased continuously from 8.1 to 41.2 μΩ cm (see Table 3) as their thickness decreased from 60 to 40.9 nm. It was noted that the films were smooth and mirror-like up to 300 °C but became dim as the temperature was increased. If the samples are cooled in a hydrogen atmosphere, carbon and oxygen admixtures in the film are virtually absent. On the other hand, cooling of the films in a nitrogen atmosphere results in a rather high content of the carbon admixture (12%–19%).

The factors determining the growth rate, the adhesion to the substrate and the morphology of the copper films obtained from $Cu(DPM)_2$ vapour in the CVD process were considered in detail by Dutta *et al.*[157] The effect of additional UV irradiation on such films was discussed:[150] at a constant substrate temperature, additional photostimulation of thermolysis decreased significantly the SER of the films (see Table 3).

The following variant of the CVD process has been suggested:[158] the vapour of the starting $Cu(DPM)_2$ was carried with a stream of nitrogen containing hydrogen and was then decomposed on a borosilicate glass substrate in the temperature range from 220 to 400 °C. In this case, the deposition of copper films was rather fast for $Cu(DPM)_2$ (26 nm min^{-1}) at a relatively low SER (1.7–2.7 μΩ cm at thicknesses ⩾ 50 nm).

2. Polyfluorinated copper(II) β-diketonates

It is known that incorporation of fluorine atoms into molecules of organic compounds generally increases their volatilities, despite the essential increase in the molecular masses. The nature of this effect is still uncertain. It is assumed that it can be due to weakening of the van der Waals interactions [111, 159] and (in some cases) due to the disappearance of hydrogen bonds upon replacement of hydrogen atoms in the molecule by fluorine atoms.[109] However, this can hardly be regarded as a comprehensive explanation.

Copper (II) β-diketonates also obey this rule.[132, 159, 160] For example, replacement of methyl groups in the $Cu(acac)_2$ molecule by trifluoromethyl groups results in a 10^4-fold increase in saturated vapour pressure of the chelate at constant temperature.[160] In addition, the thermal decomposition of polyfluorinated copper(II) β-diketonates results in films with a lower content of impurities (in particular, carbon). In most cases, the formation of copper fluorides is not observed even under rather drastic deposition conditions,[161] though the formation of CuF as a labile intermediate product is possible. This can be due both to the relative strength of the C–F bond in comparison with the C–O and

Table 3. CVD conditions and properties of copper films obtained from copper(II) β-diketonates.

Starting MCC	T /°C	T_s /°C	Carrier gas	P /Torr	Substrate	SER /μΩ cm	Ref.
$Cu(acac)_2$	–	220–250	H_2/Ar	–	SiO_2/Si	–	151
	–	220–250	H_2	–	SiO_2/Si	1.7	152
	–	350–400	H_2	–	SiO_2/Si	–	153
	110–170	< 300 [a]	H_2	–	SiO_2/Si	1.8	134
$Cu(DPM)_2$	110	350	H_2	20	SiO_2	10	133
	120	220–400	H_2/N_2	5–10	SiO_2/Si	8.1–41.2	116
	–	250–350	H_2	–	sapphire	4.6	150
	–	250–350 [b]	H_2	–	"	1.7	150

[a] In plasma. [b] Under UV irradiation.

C–C bonds and to the high stabilities and volatilities of the polyfluorinated organic products of thermolysis. Owing to these properties, polyfluorinated copper(II) β-diketonates became the first CCC utilised in the CVD technology.[110]

Copper(II) hexafluoroacetylacetonate $Cu(HFA)_2$ (**1**, $R = R' = CF_3$) is the polyfluorinated copper(II) β-diketonate studied most thoroughly and used most widely in the CVD process.[111] Copper(II) trifluoroacetylacetonate $Cu(TFA)_2$ (**1**, $R = CH_3$, $R' = CF_3$) was also considered as a starting CCC. The use of copper(II) pivaloyltrifluoroacetylmethanate $Cu(PTA)_2$ and some other substances of this series was much less common.

a. Synthesis and physicochemical properties

Polyfluorinated copper(II) β-diketonates are synthesised from the corresponding polyfluoro-β-diketones. These starting compounds were difficult to prepare[162] until they became available by the Claisen condensation.[163, 164]

$$CF_3COOEt + CH_3COR \xrightarrow[-EtOH]{EtONa} CF_3COCH_2COR$$

$R = CH_3, CF_3$, *etc.*

This reaction became a reliable source of trifluoro- and hexafluoroacetylacetone and a series of their analogues.

The classical method for the synthesis of copper(II) hexafluoroacetylacetonate $Cu(HFA)_2$ involves the reaction of copper(II) nitrate with hexafluoroacetylacetone in aqueous solution in the presence of sodium acetate (molar ratio 1 : 2 : 2).[120] This results in the precipitation of green crystals, the composition of which was determined differently by different researchers.[119, 165, 166] It is believed[120] that these are the crystal hydrates $Cu(HFA)_2 \cdot 2H_2O$ which do not decompose on sublimation. However, this conclusion was disputed later[167] and it was noted that the amount of water of crystallisation in the $Cu(HFA)_2$ hydrate is not constant. According to the results of Funck and Ortolano,[167] the green crystals are monohydrates (see also Ref. 168), since the dihydrate isolated by them was a thermally unstable yellowish-green compound. Difficulties in assigning $Cu(HFA)_2 \cdot nH_2O$ obtained by this method to mono- and dihydrates were also encountered later.[161]

Yet another method for the preparation of $Cu(HFA)_2$ is the reaction of the ammonia complex of H(HFA) with $CuCl_2$ in aqueous solution.[169] The main product in the form of bluish-green crystals was characterised as a dihydrate, its melting point coincided with that reported previously.[120] Nevertheless, these data disagree with other reported results.[167]

Yet another method for the synthesis of high-purity $Cu(HFA)_2$ with the use of H(HFA) and copper(I) oxide was patented.[170]

A drawback of the monohydrate $Cu(HFA)_2 \cdot H_2O$ as the starting compound in the CVD processes is its ability to undergo decomposition with elimination of water in the reactor at low pressures in a carrier gas stream.[171] Therefore, anhydrous $Cu(HFA)_2$ is extensively used in these processes; under standard conditions, it has the form of purple crystals which are rather hygroscopic in air.[120]

Copper(II) trifluoroacetylacetonate $Cu(TFA)_2$ was first synthesised by Schultz and Larsen[172] from the corresponding β-diketone (see also later studies[164, 173]). A procedure for its preparation with the use of ammonium β-diketonate was reported.[169] Many fluorine-containing copper(II) β-diketonates [including $Cu(TFA)_2$] and the corresponding β-diketones have been obtained by Park *et al.*[174]

Generally, $Cu(TFA)_2$ and $Cu(HFA)_2$ are much more volatile than their analogues with alkyl groups described in the previous section.[175–177] Futhermore, they were found to be the most volatile in a large series of fluorine-containing copper(II) β-diketonates, as indicated by thermogravimetric data.[178] The vapour pressure of $Cu(HFA)_2$ measured by various methods[179, 180] is 3 Torr at room temperature and atmospheric pressure.[181]

The initial study of the decomposition of $Cu(TFA)_2$ and $Cu(HFA)_2 \cdot H_2O$ vapour in the CVD process showed that the sublimation of these CCC occurs at 85 and 65 °C, respectively.[110] The standard enthalpy of evaporation of $Cu(HFA)_2$ is 13.2 ± 0.8 kcal mol^{-1} (see Ref. 180).

The β-diketonates of divalent copper containing the n-heptafluoropropyl group are rather exotic but quite suitable for the preparation of thin copper films by CVD. These compounds include such chelates as copper 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate $Cu(FOD)_2$ (**1**, $R = Bu^t$, $R' = n\text{-}C_3F_7$)[182] and copper 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dionate $Cu(FND)_2$ (**1**, $R = R' = n\text{-}C_3F_7$). These β-diketonates can be synthesised from β-diketones by the usual method.[183]

Stabnikov *et al.*[184] studied the possibility of synthesis of mixed-ligand copper(II) β-diketonates where the copper atom is simultaneously bound to diketones with alkyl (acac, DPM, *etc.*) and fluorinated alkyl groups (TFA, HFA). The crystal and molecular structures of some of these compounds were studied.[160, 185–187] It was shown that they have intermediate properties between those of 'homogeneous' bisdiketonates incorporating the corresponding ligands; in the vapour phase, mixed-ligand compounds can undergo disproportionation to give homogeneous bisdiketonates. It was therefore concluded that these compounds have no advantages which would make them promising for practical use in CVD technologies.[184]

b. Mechanisms of decomposition on the substrate surface

The thermal decomposition of $Cu(HFA)_2$ vapour in CVD processes and its products have been studied in detail.[139, 188, 189] It was shown that H(HFA) is the main decomposition product of $Cu(HFA)_2$ in the vapour phase, while thermal decomposition on a SiO_2 surface at 480 °C can give either a CuO film (in air) or a film of metallic copper with small admixtures of Cu_2O and HFA decomposition products (in an argon atmosphere). The main decomposition product in air at 800 °C is Cu_2O in the form of finely dispersed particles.

As shown by Lecohier *et al.*,[190] the growth of a copper film from $Cu(HFA)_2$ vapour involves several stages. During an induction period, the duration of which depends on the properties of the substrate surface and on the deposition method, film growth is not observed. Subsequently, the formation of isolated copper islets starts. Their merging results in a sharp decrease in the SER.

Van Hemert *et al.*[110] suggested a mechanism of copper reduction from its chelate in a hydrogen atmosphere; this mechanism can be expressed by the overall equation

$$Cu(\beta\text{-diket})_2 + H_2 \longrightarrow Cu + 2\,H(\beta\text{-diket})\uparrow .$$

In the case of copper(II) β-diketonate hydrates, the formation of precursors in hydrated form was postulated.

A similar decomposition equation was suggested for the thermolysis of $Cu(HFA)_2$ at relatively low temperatures (below 340 °C).[180]

Thus, it is believed that thermolysis of the compounds in question starts with the cleavage of the copper–oxygen bonds. It was noted that at higher temperatures (500–600 °C) cleavage of the C–C bonds in the ligand also occurs and results in carbon admixtures in the film.

These concepts are basically correct but they do not provide a sufficiently full description of the processes occurring when the molecules of the starting CCC reach a heated substrate surface. A detailed scheme of these processes was developed somewhat later and generalised by Kim *et al.*[191]

The following assumptions were used in the description of the mechanism of transformations in the CVD processes: the CCC and hydrogen molecules are adsorbed on different sites of the substrate surface; the adsorption of molecules of CCC competes with that of the original β-diketone formed upon reduction; the reduction occurs on the substrate rather than in the gas phase.

A scheme consisting of five basic steps was suggested based on these assumptions:

(1) adsorption of molecules of CCC with their partial dissociation

$$Cu(HFA)_2 + 2A^* \longrightarrow Cu(HFA)A^* + (HFA)A^*;$$

(2) disproportionation of partially adsorbed copper(I)-containing intermediates

$$2Cu(HFA)A^* \longrightarrow Cu + Cu(HFA)_2A^*,$$

or

(2′) progression of dissociation of the intermediate copper(I) derivative

$$Cu(HFA)A^* \longrightarrow Cu + (HFA)A^*;$$

(3) dissociative adsorption of hydrogen

$$H_2 + 2B^* \longrightarrow 2HB^*;$$

(4) formation of a volatile product, *viz*., a β-diketone, on the surface

$$(HFA)A^* + HB^* \longrightarrow H(HFA)A^* + B^*;$$

(5) desorption of the β-diketone

$$H(HFA)A^* \longrightarrow H(HFA)\uparrow + A^*.$$

Here A* and B* indicate the active sites of, initially, the substrate and, later, the growing copper film capable of chemisorption.[192] Step 4 is the limiting step of the entire process.[192, 193]

A somewhat simplified version of this mechanism was suggested earlier.[194] It was noted that the irreversibility of the entire process begins in the step where metallic copper adsorbed on the substrate appears. The copper atoms form microclusters on the substrate surface, which consist of 8–12 copper atoms and are clearly separated from the organic ligands.[195]

Certainly, the temperature of the process and the material of the substrate affect the course of the steps considered. A study of the thermodynamic parameters of the thermal decomposition of $Cu(HFA)_2$ and the phase compositions of the copper films formed in a rather broad temperature range showed that copper(I) fluoride can be formed in one of the intermediate steps at rather low temperatures. This is not taken into account in the scheme suggested above. As the temperature increases, the amount of CuF decreases until it disappears completely.[196]

The effect of the substrate material on the mechanism of thermolysis of $Cu(HFA)_2$ vapour was analysed in detail.[197] It was noted that decomposition of $Cu(HFA)_2$ in a stream of H_2 on a TiN surface can result in replacement of fluorine atoms in the trifluoromethyl group by hydrogen atoms. In the case of the SiO_2 substrate, a noticeable amount of CF_3COOH is formed, which is the product of cleavage of the C–C bonds in the HFA fragment.

Let us outline the applicability limits of the mechanism considered. Two types of CVD processes are distinguished, depending on the conditions.[198] At rather low temperatures and partial vapour pressures of the starting CCC, the process is primarily characterised by reactions on the substrate surface occurring in accordance with the mechanism described above (the so-called reaction-limited conditions). At high substrate temperatures and pressures in the reactor and at high vapour pressures of the substance, this mechanism does not operate and the film deposition process is characterised by the transport of molecules of CCC to the substrate (transport-limited conditions). These conditions generally result in film heterogeneity.[198]

In order to reveal the details of the thermal decomposition mechanism of $Cu(HFA)_2$ on various substrates, some authors used ultrahigh vacuum conditions ($\leqslant 10^{-7}$ Torr). Such conditions are unlikely to be suitable for industrial CVD processes, but we feel that the results obtained should be discussed.

If thermal decomposition of $Cu(HFA)_2$ vapour during CVD is carried out in ultrahigh vacuum, the process mechanism changes essentially. In this case, disproportionation of the intermediate copper(I) derivative does not occur.[199] For example, the $Cu(HFA)_2$ molecules are quickly desorbed from the TiN substrate at as low temperature as 75 °C, and further decomposition of the intermediate [reaction (2′), see above] becomes the dominating process. At 200 °C, decomposition of the adsorbed ligand begins to give CO, CO_2 and CF_4; as a result, ~ 30% of Cu from the starting material remains on the substrate.

Disproportionation of copper(I) intermediates is not observed, either, in the deposition of copper films onto polycrystalline tantalum substrates from $Cu(HFA)_2$ vapour.[200] It was noted that adsorption of CCC on a tantalum surface starts at 158 °C; formation of a copper film occurs at temperatures $\leqslant$ 117 °C, while diffusion of copper into tantalum is observed at 477 °C.

The adsorption of $Cu(HFA)_2$ molecules and their subsequent decomposition on the (100) and (111) surfaces of copper single crystals in ultrahigh vacuum (10^{-10} Torr) have been studied.[201] It was shown that under these conditions, surface migration of ligands of the adsorbed molecules of CCC with formation of isolated HFA groups adsorbed on the substrate parallel to its surface occurs even at low temperatures (~ −73 °C). At 102 °C, their decomposition gives CO, CO_2 (quickly desorbed from the substrate), CF_3 and the ketenylidene fragments C=C=O adsorbed through the terminal carbon atom. At temperatures above 227 °C, the CF_3 species are desorbed, while the C=C=O fragments undergo decarbonylation; the carbon remaining on the surface is the basic source of film contamination.

As shown for the adsorption of $Cu(HFA)_2$ on a platinum surface under similar conditions,[202] the orientation of HFA groups depends on the thickness of the layer of molecules of CCC adsorbed on the substrate. Ligand orientation parallel to the substrate surface is characteristic of very thin films; as their thickness increases, the ligands are 'reoriented' to become perpendicular to the substrate. It was also noted that difluorocarbene CF_2 is the most strongly adsorbed species, which is desorbed in ultrahigh vacuum only at 577 °C.

The nature of interaction of $Cu(HFA)_2$ and the β-diketone H(HFA) itself with the surface of the SiO_2 substrate was studied in detail.[203] The experiments were carried out in ultrahigh vacuum (5×10^{-8} Torr). In this case, everything is determined by the presence of OH groups, both isolated and connected by hydrogen bonds, and siloxane bonds, Si–O–Si, on the surface of the substrate. It was shown that preferential adsorption of $Cu(HFA)_2$ molecules at 25 °C occurs with involvement of isolated surface OH groups. On heating the substrate (studied in the range up to 400 °C), decomposition of adsorbed $Cu(HFA)_2$ was observed; in this case, the OH groups involved in the adsorption were not recovered.

Farkas *et al*.[203] reported experiments aimed at decreasing the density of OH groups on a SiO_2 surface as a result of its thermal treatment. It was found that in this case strong adsorption of the $Cu(HFA)_2$ molecules involves surface siloxane bonds, which are cleaved irreversibly upon subsequent heating and thermolysis of $Cu(HFA)_2$. However, desorption of the decomposition products occurs at rather high temperatures, *viz*., about 400 °C irrespective of pretreatment of the SiO_2 surface. The mechanism suggested by the authors involves direct axial coordination of the copper(II) atom with the non-shared electron pairs of the oxygen atoms of the OH groups or the Si–O–Si bonds, giving a five-coordinate complex. A similar explanation was suggested previously for the interaction of $Cu(acac)_2$ with a SiO_2 surface.[204]

The deposition mechanism of copper films from $Cu(HFA)_2$ vapour in the presence of water vapour was considered in detail.[205–208] It was assumed that intermediate formation of a $Cu(HFA)_2$ mono- or dihydrate occurs in the gas phase

$$Cu(HFA)_{2\,(vapour)} \xrightarrow{H_2O} Cu(HFA)_2 \cdot H_2O_{(vapour)}.$$

In the resulting complex (under gas-phase conditions) an intramolecular transfer of H_2O protons to the ligand occurs, which weakens the copper–oxygen bonds. Adsorption of this complex on the surface results in elimination of the hydrated enol form of the β-diketone

$$Cu(HFA)_2 \cdot H_{2(vapour)} \longrightarrow Cu(HFA)_2 \cdot H_{2(ads)} \longrightarrow$$
$$\longrightarrow Cu^{2+}_{(ads)} + 2\,(HFA) \cdot H_{2(ads)}\,.$$

The adsorbed Cu^{2+} ions are reduced under the action of hydrogen.

Since reduction is the limiting step of the process, the side formation of copper(I) oxide is observed at low deposition temperatures.[209, 210] It was found with the use of the ^{18}O isotope that the formation of an oxide phase involves the oxygen atoms of H_2O rather than those of the H(HFA) ligand.[209] However, in general, the addition of water vapour to the carrier gas in an optimum temperature mode does not result in contamination of films with copper oxides. This is believed to be due to the fact that the reduction of copper

$$Cu_2O + H_2 \rightleftharpoons 2\,Cu + H_2O$$

is an exothermic process (the equilibrium constant is 0.78×10^8 at 325 °C).[205]

The presence of water vapour in the carrier gas improves the morphological characteristics of the films. This can be due to the fact that the nucleation rate of copper is determined by the rather low activation energy for decomposition of the adsorbed $Cu(HFA)_2$ hydrate and hence almost does not depend on the properties of the substrate surface. Owing to the high density of the nucleation centres determined by the amount of the adsorbed hydrate, smooth films with good morphology are formed. On the other hand, the formation of film nuclei in usual systems is limited by a surface reaction between the adsorbed molecules of anhydrous CCC and hydrogen, the rate of which depends on the density of the adsorption centres on the substrate surface. In this case, the film is very sensitive to the quality of the substrate.[205]

The role of molecules of an alcohol in the deposition of copper films from vapour of solutions of the starting CCC in the alcohol is somewhat similar to the role of water molecules.

Like water, methanol and ethanol in the vapour phase can be coordinated with the copper(II) ion in copper β-diketonate; as a result, molecules of the complex of copper β-diketonate with the corresponding alcohol are deposited on the substrate.[208] The proton of the alcohol molecule in the adsorbed complex can then be transferred to the adsorbed HFA ligand obtained due to the CCC decomposition; this favours the desorption of an H(HFA) molecule from the substrate surface. An adsorbed alkoxy group that remains on the surface can be removed by two pathways: either by elimination of the hydrogen atom from the α-carbon atom to give a volatile carbonyl compound, or by the reaction with the adsorbed hydrogen atom from the carrier gas to give the alcohol.[211, 212] In the former case, the alcohol acts as a reducing agent, while in the latter case, as a reduction catalyst. Propan-2-ol is the most efficient compound,[213] in spite of the fact that propan-2-olic complexes of copper β-diketonates are the least stable complexes with alcohols.[208]

The mechanism of photochemical deposition of copper films from the vapour of CCC under laser irradiation of substrates was suggested and considered in detail by Ehrlich and Tsao.[214] Special attention was given to film growth rate simulation.

A study by Zheng *et al.*[215] dealt with the mechanism of $Cu(HFA)_2$ vapour decomposition in a stream of hydrogen under exposure to plasma. It was shown that under these conditions preferential consecutive elimination of CF_3 groups from the ligand is observed, rather than elimination of the entire ligand with cleavage of the Cu–O bonds. Nevertheless, this decomposition pathway also gives only volatile organic products which do not contaminate the film obtained.

The thermodynamics of decomposition of $Cu(HFA)_2$ and its analogue, $Cu(FOD)_2$, in the PACVD process has been considered.[216]

The authors of the first studies on the PACVD method for the preparation of copper films assumed that the role of plasma involves the formation of a high concentration of reactive hydrogen species.[155, 216, 217] However, the details of the mechanism remained unclear. A model of decomposition of $Cu(HFA)_2$ with the use of hydrogen plasma was described.[193] It was noted that in this process the hydrogen plasma is mainly electropositive and consists of cations, *i.e.*, H^+, H_2^+ and H_3^+, electrons and hydrogen atoms. The overall process occurs according to the five-step mechanism discussed above; however, both the hydrogen atoms adsorbed on the substrate and the hydrogen atoms from the gas phase can participate in the limiting fourth step. The film quality and the deposition rate are determined by the pressure in the reactor, the electric field power and the substrate temperature. At small power (up to 25 W), the following kinetic equation is valid:

$$R_d = k[Cu(HFA)_2]^{1/2}[H]\,,$$

where R_d is the rate of the direct deposition reaction, k is the rate constant of the limiting (fourth) step. At high electric field power, decomposition of HFA fragments starts, the process becomes more complicated and strong contamination of films with carbon and fluorine is observed.[193]

The decomposition mechanisms of other fluorinated copper(II) β-diketonates in CVD processes have almost not been studied. It was shown[189] that H(FOD) is the main product of $Cu(FOD)_2$ decomposition in the vapour phase. One can also mention a study of the kinetics of thermal decomposition of $Cu(PTA)_2$ vapour upon heating of the substrate with a CO_2 laser;[218] the observed phenomena are in full agreement with the concepts of the reaction-limited and transport-limited processes as a function of deposition conditions. Data are available on the products of $Cu(FND)_2$ thermolysis and its behaviour under CVD conditions in the presence of vapour of water and alcohols.[208]

c. Preparation and characteristics of copper films

In the first experiments on the preparation of thin copper films by CVD based on decomposition of $Cu(TFA)_2$ and $Cu(HFA)_2 \cdot H_2O$ vapour in a stream of hydrogen under atmospheric pressure, the optimum temperature of glass substrates on which films are formed was found to be 250 °C. However, the characteristics of films were not reported.[110] The decomposition was purely thermal, without additional activation with laser radiation or plasma. A little later, a similar procedure was patented by the same authors.[219]

The process of non-activated thermal deposition of copper films from $Cu(HFA)_2$ vapour was also studied in a number of works (see, *e.g.*, Refs 40, 115, 180, 191, 194, 219–244).

Typical conditions were used by Kim *et al.*:[191] the pressure in the reactor was 10 Torr, the temperature of the $TiSi_2/Si$ substrate was 300–400 °C, an H_2/Ar mixture (3 : 1) was used as the carrier gas (Table 4). It was found that at low pressure and with this substrate material, no growth of the copper film on the substrate occurred at temperatures up to 300 °C. Above this temperature, the growth rate was 10–100 nm min^{-1}. The film thickness depended linearly on the deposition rate, *i.e.*, the deposition rate was practically the same in each experiment. As the hydrogen partial pressure in the carrier gas was decreased, a considerable decrease in the deposition rate was observed. The surface morphology of the films obtained under these conditions was studied in detail.[220, 223]

The deposition of copper films by decomposition of $Cu(HFA)_2$ vapour on SiO_2/Si substrates in the temperature range from 250 to 650 °C in the absence of hydrogen (with pure argon as the carrier gas) was studied by Temple *et al.*,[180] who did not observe the formation of films at 250 °C, as opposed to the results of other studies.[110] Pure copper films appeared in the

Table 4. CVD conditions and properties of copper films obtained from polyfluorinated copper(II) β-diketonates.

T /°C	T_s /°C	Carrier gas	P /Torr	Substrate	SER /μΩ cm	Ref.
Starting CCC — $Cu(HFA)_2$						
–	300 – 400	Ar/H_2	10	$TiSi_2/Si$	2.0	191
–	300 – 400	Ar	10	TiN/Si TiW/Si	2.0	221, 222
–	–	–	–	Cr (on Si)	1.7	224
97 – 120	340 – 390	Ar	8 – 10	SiO_2/Si	3 – 7	180
–	250 – 300	H_2/Ar	0.75	Si, SiO_2	1.9	115
–	250	H_2/He	2 – 10	glass	2 – 3	194
80 – 100	160 – 170 [a]	H_2	1 – 1.7	Si, Ti, W	1.7 – 1.9	244
65 – 85	310 – 390	H_2	15	Au/Si	2.5 ± 0.3	218
65 – 90	310 – 390	H_2/Ar	2 – 20	SiO_2, $TiSi_2$	2.0 ± 0.1	220
60	300 – 400	H_2	0.15	SiO_2/Si	–	199
–	800 [b]	–	–	–	3.6 ± 0.1	236
60	400[c]	He/H_2O	0.075	SiO_2/Si	2	190
75 – 94	350 – 410	H_2/H_2O	15	Ta/SiO_2	2.0	205
65 – 85	310 – 390	H_2/Ar	2 – 10	SiO_2/Si, $TiSi_2$	2.0 – 2.3	223
100	130 – 200[c]	H_2/Ar	760	SiO_2/Si	–	241
95 – 98	300	H_2	1 – 10	TiN/Si	2.5 – 5	211
–	230 [a]	H_2	2	SiO_2, Si, Al	2.0	243
–	160 – 170 [a]	H_2	–	SiO_2/Si W/Si	1.7 – 1.9	244
80	225 [a]	H_2/Ar	1	Si	1.7	215
Starting CCC — $Cu(FOD)_2$						
–	< 250	H_2	1 – 10	SiO_2, Si, Al	3.0	182
–	300 – 400	H_2	1 – 10	SiO_2, Si, Al	1.8	182

[a] In plasma. [b] Under laser irradiation followed by cooling to 250 °C. [c] Under laser irradiation.

temperature range of 340 – 390 °C (see Table 4). Upon further heating of the substrate to 430 °C, the films containing 65% of carbon (25% of copper) were formed, while the films obtained at 500 °C consisted of pure carbon.

In other studies, the temperature range for the formation of pure copper films by decomposition of $Cu(HFA)_2$ vapour in argon was somewhat wider, *viz*., from 310 to 400 °C.[221, 222] Films of rather high quality were obtained with a growth rate of 65 nm min^{-1}. It was noted that the substrate (TiN, TiW) surfaces had to be cleaned from oxide contaminants.[222]

Awaya and Arita [224] synthesised copper films from $Cu(HFA)_2$ vapour on a Si substrate coated with a few buffer layers at once (the top layer consisted of chromium, see Table 4). Such films had low SER values and contained an admixture with chromium.

In addition to hydrogen, water can be used as a reducing agent for $Cu(HFA)_2$.[171, 190, 205, 225, 226] In this case, the growth rate of copper films depends directly on the amount of water vapour in the gas phase.[225] The presence of water vapour during the decomposition of $Cu(HFA)_2$ vapour increases considerably the film growth rate (approximately by two orders of magnitude [171]) but the selectivity of the process decreases (see Section VI). The specifics of the film growth kinetics in this method and the film morphology were considered in detail.[190] It was reported [171] that the SER of the resulting films can be as low as ~ 2.0 – 2.1 μΩ cm while the deposition rate remains high.

Another group of researchers who studied a similar process suggested the use of $Cu(HFA)_2$ dihydrate rather than $Cu(HFA)_2$ as the starting CCC.[205] They reported a high deposition rate and good morphology of the copper film surfaces. However, the results of this study were poorly reproducible, probably due to the instability of the dihydrate; it was reported that this substance readily eliminates water molecules in the vapour phase.[227] The use of anhydrous $Cu(HFA)_2$ in the presence of water vapour gave films with low SER (deposition rates up to 90 nm min^{-1}).

An interesting modification of the method considered above involves the deposition of copper films from the vapour phase of a CCC solution in an alcohol.[211] It is known that anhydrous $Cu(HFA)_2$ is freely soluble in alcohols (ethanol, propan-2-ol). In this method, a stream of the carrier gas (H_2) is passed through an ~ 0.4 g ml^{-1} alcoholic solution of $Cu(HFA)_2$ (higher concentrations result in an increased solution viscosity and, as a consequence, instability of the process). The alcohol vapour present in the gas phase serves as an additional reducing agent.

The advantage of this technique is the significant (approximately fivefold [211]) increase in the deposition rate of copper films in comparison with that in the usual process in a stream of hydrogen. However, the films obtained using this technique have higher porosity which inevitably impairs their properties. For example, the SER of copper films synthesised by Borgharkar *et al*.[211] was 2.5 – 5 μΩ cm (see Table 4) provided that their thickness was no less than 1000 nm. The characteristics of these films can be improved by addition of water vapour to the carrier gas; in this case, the SER of the films was 2.6 – 2.9 μΩ cm.[211] A technique for CVD of copper films from CCC with participation of a solvent has been patented.[228]

Attempts at performing the CVD process with $Cu(HFA)_2$ with an excess of the starting β-diketone H(HFA), which in turn is a decomposition product of the precursor, were reported. It was noted [194] that the excess of H(HFA) decreased the copper film deposition rate. Nevertheless, if SiO_2 templates deposited on a copper substrate were used for the preparation of thin copper strips from $Cu(HFA)_2$, pretreatment of the template channels with H(HFA) vapour improved considerably the characteristics of the strips, but the presence of H(HFA) vapour during the deposition process is unacceptable as it caused an abrupt impairment of the strip morphology and a loss of selectivity.[229]

It is known that polyfluorinated copper(II) β-diketonates are photo-labile compounds. Their photochemistry in solution [230] and in the gas phase [231 – 233] has been studied rather thoroughly. Laser irradiation of the substrate is a popular method for decomposition of the vapour of these compounds for deposition on substrates.[181, 232, 234 – 238] In this case, $Cu(HFA)_2$ itself or its alcoholic solution (an 'alcoholic' CVD technique) can be utilised for the preparation of films.

This creates certain difficulties. First, it is difficult to estimate to what degree the observed process is pyrolytic and to what

degree it is photochemical, as the substrate temperature is ~ 250 °C,[236] and it is difficult to estimate accurately the temperature of the process in laser experiments.[239] It is known that the quantum yield of decomposition of copper(II) β-diketonate vapour to the metal is rather small; this determines the low film growth rates by the purely photochemical mechanism and the irregularity of their morphology. Second, photochemical decomposition can increase the content of the carbon admixture in the copper film; fluorine and oxygen are removed with the volatile photolysis products.[234] It was shown in experiments on copper film deposition under laser irradiation with a wavelength corresponding to the visible spectrum range that carbon is a photolytic admixture in this case; under these conditions, the carbon contamination of the films was absent.[236]

A thorough refinement of the photochemical process modes for the deposition of films was required to overcome the difficulties noted above.[237, 240] In a study devoted to the effect of laser power on the growth rate of copper films from $Cu(HFA)_2$ vapour,[241] the deposition rate was increased from 20 to 120 nm min^{-1} in a stream of an argon–hydrogen mixture and from 4 to 27 nm min^{-1} in a stream of argon, but the SER of the films were not reported. It was noted that in the presence of ethanol under laser activation conditions, as in the usual thermolysis, the growth rate of copper films increased.[234, 238]

The properties of films obtained with the use of a laser were analysed by Hoyle *et al.*[236] The films were formed on a silicon substrate at ~ 800 °C (the power density of laser radiation was 4×10^5 W cm^{-2}). As the film grew, the substrate temperature decreased gradually to 250 °C, *i.e.*, the optimum value for $Cu(HFA)_2$ vapour decomposition. The films had good adhesion properties but rather high SER values (see Table 4).

The preparation of film microstructures (copper microstrips) from $Cu(HFA)_2$ vapour is a promising field of application of the CVD process with the use of laser radiation. The optimum conditions of the process for the preparation of strips 2 mm long were chosen and the factors determining their basic characteristics were studied.[240]

A milder way of photochemical decomposition of $Cu(HFA)_2$ vapour is the use of UV irradiation.[242] In this case, the level of contamination of copper films is much lower.

Yet another method for activation of decomposition of $Cu(HFA)_2$ vapour is the use of plasma.[161, 243, 244] It was shown in the very first study on this technique that if the process is carried out in a stream of hydrogen, high-quality thin copper films could be obtained virtually without carbon admixtures by varying the source power and the substrate temperature.[161] The SER of the best film samples, 60–80 nm thick, were within 1.7–2.4 μΩ cm; these values could not be reached with laser radiation. This can be due to the fact that efficient growth of films in the plasma method requires a considerably lower source power; an increase in the power immediately resulted in carbon contamination.

Plasma activation was used to improve considerably the characteristics of the copper films obtained by the 'alcoholic' method. For example, decomposition of the vapour of an ethanolic solution of $Cu(HFA)_2$ in a stream of hydrogen at a plasma source power of 45 W gave a copper film 63 nm thick with a low SER (see Table 4).[243] An optimum content of hydrogen in the carrier gas is a prerequisite for the preparation of high-quality copper films by this method: at a hydrogen concentration lower than 88%, the SER of copper films increased to 9–10 μΩ cm. An opposite relationship was observed for the grain size in the copper film: a decrease in the fraction of hydrogen in the carrier gas decreased the grain size from ~ 100 (88% H_2) to ~ 10 nm (0% H_2). The reasons for this phenomenon were not rationalised.

Copper films with good characteristics were obtained [244] using a similar technique by decomposition of the vapour of $Cu(HFA)_2$ solutions in ethanol and propan-2-ol at relatively low substrate temperatures and a power density of the plasma source of 0.13–0.25 W cm^{-2}. A high film growth rate, *viz.*, 25 nm min^{-1}, was reported; the SER of films 440 nm thick was 1.7–1.9 μΩ cm. Polycrystalline copper films 500–1000 nm thick were obtained from the vapour of a rather rare starting CCC, *viz.*, $Cu(FOD)_2$.[182] The resulting copper film (argon as the carrier gas) contained up to 24% admixtures (C, O, F). Replacement of argon with hydrogen resulted in a pure copper film with good characteristics; in this case, a decrease in the substrate temperature (to 250 °C and lower) increased the SER of the films considerably (see Table 4).

3. Complexes of copper(II) β-diketonates with additional ligands

The copper atom in copper(II) β-diketonates is coordination-unsaturated, hence it is possible to synthesise adducts of copper(II) β-diketonates with various organic Lewis bases (primarily, nitrogen- and oxygen-containing ones). Some of these adducts are volatile. However, the prospects of their use in the CVD technology as precursors are doubtful.

Unlike copper(I) β-diketonates, copper(II) β-diketonates are convenient starting CCC for the CVD technology. As a rule, it is easier to change their properties by modifying the starting β-diketone than to try to obtain a stable adduct with an additional ligand which can be sublimed.

Nevertheless, the use was suggested of some compounds of this type as volatile CCC, for example, the adduct of $Cu(DPM)_2$ with *o*-phenanthroline (1 : 1), which is sublimed *in vacuo* at 130 °C without decomposition.[245] Under the same conditions, $Cu(DPM)_2$ itself is sublimed at 160 °C. It was reported that an attempt at sublimation of a similar $Cu(acac)_2$ adduct resulted in its decomposition.

The 1 : 1 adducts of $Cu(HFA)_2$ and $Cu(PTA)_2$ with *o*-phenanthroline and 2,2′-bipyridyl are also volatile.[246] However, the sublimation temperatures for all four adducts exceed 160 °C, which is higher than those for the original copper β-diketonates.

More promising in this respect is the synthesis of a series of volatile adducts of $Cu(HFA)_2$ with ethanolamines.[247] As noted above, the addition of ethanol vapour to the carrier gas increased the copper film deposition rate. It was assumed that the ethanolamine adducts obtained, which contained a 'preformed' ethanol fragment, will maintain this advantage; on the other hand, the presence of the amino group should impart stability to the adduct under sublimation conditions.

Preliminary CVD experiments on this type of copper(II) derivatives showed that the adduct of $Cu(HFA)_2$ with 1-dimethylaminopropan-2-ol, which forms a copper film at a substrate temperature of 300 °C, has quite satisfactory characteristics suitable for CVD processes.[247] However, the parameters of the process and the film characteristics were not reported. No films were obtained with the use of a similar adduct with ethanolamine.

4. Other classes of volatile compounds of copper(II)

The range of volatile organic derivatives of copper(II) suitable for CVD processes is not limited to β-diketonates, but the choice is rather narrow.

a. Chelate complexes, analogues of copper(II) β-diketonates

Nitrogen-containing analogues of β-diketones (iminoketones) form volatile derivatives of copper(II) with physicochemical properties satisfactory for CVD processes.[248] Nevertheless, we could find only one study devoted to the practical preparation of copper films from this class of compound.[249] A new compound synthesised by the authors, *viz.*, bis[4-(2,2,2-trifluoroethyl)imino-1,1,1,5,5,5-hexafluoropentan-2-onato]copper(II) designated as $Cu(nona\text{-}F)_2$, had a decomposition temperature of 270 °C. Copper films with satisfactory characteristics were obtained from this compound but no further developments were reported.

Of compounds the structure of which is somewhat similar to that of copper β-diketonates, chelate complexes of copper(II) with analogues of ethyl acetoacetate (CH_3COCH_2COOR) can be considered as a real alternative to the former. A series of these compounds (R = Me, Et, Bu^t, CH_2Ph and $CH_2CH_2OCH_3$), their hydrates and adducts with alcohols were synthesised [250] using a

technique similar to that used for copper β-diketonates.[120] The sublimation temperatures of these compounds were from 78 to 113 °C at 0.16 Torr. The crystal structure of $Cu(CH_3COCHCOOBu^t)_2$ monohydrate was determined.[136]

CVD experiments with compounds of this series at low pressures (0.1 – 1 Torr) in the presence of hydrogen resulted in high-quality copper films with SER values ranging from 1.8 to 2.5 μΩ cm; in addition, the factors determining their adhesion to the substrate were studied.[250, 251] A Si substrate with a TiN or TiW barrier layer was used; the deposition rate varied from 0.5 to 20 nm min^{-1} at substrate temperatures from 160 to 330 °C. Judging by the characteristics of the films obtained, $Cu(CH_3COCHCOOCH_2CH_2OCH_3)_2$ was the best starting CCC in this series.[250]

If copper(II) ester chelates are used, copper films are formed at a relatively low substrate temperature (160 °C). For comparison: the minimum substrate temperature is 310 °C for $Cu(HFA)_2$.[220, 223] This is an important advantage of copper(II) ester chelates in comparison with copper(II) β-diketonates. No noticeable thermolysis of the adsorbed free ligands occurs at 160 °C; this ensures that the films are not contaminated.

The surface morphology of copper films synthesised by the CVD method from $Cu(CH_3COCHCOOBu^t)_2$ vapour was studied in detail.[252] Comparison of the deposition processes and microstructures of copper films obtained from $Cu(DPM)_2$ and $Cu(CH_3COCHCOOBu^t)_2$ showed that dense, crack-free films are formed from both CCC at substrate temperatures up to 350 °C, but the substrate temperature required for the deposition is about 100 °C lower in the case of $Cu(CH_3COCHCOOBu^t)_2$.[253, 254] The growth rate of the copper film from $Cu(CH_3COCHCOOBu^t)_2$ vapour is several-fold smaller, but the film structure is much better than that of the film obtained from $Cu(DPM)_2$ vapour. In another study by the same scientific group,[117] the SER of copper films synthesised from $Cu(CH_3COCHCOOBu^t)_2$ at 225 °C was reported to be 2.5 – 4.0 μΩ cm at a film thickness of 50 – 120 nm.

$Cu(CH_3COCHCOOEt)_2$ is also believed by many authors to be a promising starting CCC for the deposition of copper films. For example, dense fine-grain copper films ⩾95 nm thick were obtained from this compound at 225 °C (on a SiO_2 substrate) in a hydrogen atmosphere;[255] the SER of these films was close to that of metallic copper. This compound was also used[256] in a CVD process with plasma activation giving a copper film > 250 nm thick with a SER of 2.0 μΩ cm. The same work also reported the preparation of a 256 Mb RAM chip by CVD using decomposition of $Cu(CH_3COCHCOOEt)_2$ vapour.

b. Copper(II) carboxylates

Copper(II) carboxylates that are more readily accessible synthetically than copper β-diketonates could become a real alternative to the latter in CVD processes. However, the use of this class of substances, first of all copper(II) formate $Cu(HCOO)_2$, for the preparation of copper films was originally limited to deposition from liquids and aerosols.[63, 257, 258]

Nevertheless, it was shown subsequently that $Cu(HCOO)_2$ hydrate can be directly used in the CVD process.[259, 260] Preparation of copper films from the vapour of this compound was carried out on Si(100) and TiN substrates at 200 – 350 °C with and without a carrier gas (H_2, Ar). The highest-quality crystalline copper films without oxygen admixtures were obtained at a substrate temperature of ~ 300 °C.

Of copper carboxylates intended as potential starting CCC, volatile complexes of copper(II) polyfluorocarboxylates with 1,4-dioxane were also obtained; these compounds can sublime without decomposition at 120 – 130 °C (0.05 Torr).[261]

c. Copper(II) alkoxides and their derivatives

Volatile alkyl derivatives of copper[262, 263] cannot be regarded as technologically suitable compounds, both with respect to their synthetic accessibility and properties. Alkoxide derivatives of divalent copper are much more stable and accessible.

The simplest copper(II) alkoxides of the type $Cu(OR)_2$, where R = Me, Et, *etc*., are unsuitable for CVD processes because they are polymeric non-volatile compounds.[264] Compounds obtained by partial replacement of hydrogen atoms in Cu(II) alkoxides by fluorine atoms sublime at 80 – 90 °C. Their thermal decomposition occurs at 140 – 200 °C,[265] but these compounds have not been studied from the viewpoint of their use in CVD technology. Attempts were made to synthesise monomeric alkoxides as the starting compounds for CVD processes.[266, 267] In fact, a series of convenient compounds [*e.g*., $Cu(OCH_2CH_2NR_2)_2$, where R = Me, Et] which sublime *in vacuo* at 60 – 110 °C were obtained, but no experiments on the preparation of copper films using CVD from them as the starting CCC were carried out.

An interesting development of this line of research was a rather simple synthesis of volatile complexes of copper(II) fluoroalkoxides with various nitrogen-containing Lewis bases with general formula $Cu(OR)_2 \cdot L$, where R is hexafluoroisopropyl $CH(CF_3)_2$ (HFIP) and $C(CH_3)(CF_3)_2$, while L = *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMED) and 2,2′-bipyridyl.[268] These complexes are monomeric and undergo sublimation with partial decomposition. However, it was shown that decomposition of vaporised $(HFIP)_2Cu(TMED)$ complex on silicon substrates at 300 °C gives a copper film with an admixture of < 1% carbon. However, in the authors' opinion,[268] the search for starting compounds which would be more competitive with copper β-diketonates among this class of compounds is necessary.

V. The starting copper-containing compounds: copper(I) derivatives

Disproportionation to copper(II) derivatives and metallic copper is one of the main reactions of copper(I) compounds. It is no wonder that this process attracted the attention of researchers in the field of preparation of thin copper films by the CVD process.

It is known that it is more difficult to synthesise volatile copper(I) derivatives than similar compounds containing copper(II). However, studies in the field of CVD processes with the use of monovalent copper compounds, which have started rather recently, are very intense.[111, 269] This is due to the fact that thermally induced disproportionation has certain advantages over thermal decomposition.

These advantages include the following: the process occurs with higher deposition rate and at lower temperatures; the ligands bound to the Cu(I) atoms are removed in a more favourable temperature range without decomposition to volatile products. This provides good technological characteristics: the process is safer as generally there is no need to use a carrier gas and hydrogen as the reducing agent; a high-purity film grows because it is not contaminated with carbon, fluorine and oxygen. These advantages expand the prospects and reduce the restrictions related to the design and control of the technological process of selective deposition of copper films.

It should be noted that in the case of CVD processes involving copper(I) derivatives, a certain competition exists between the CCC with organic ligands and the starting inorganic CCC (usually, copper halides).

Attempts were made to use copper(I) halides for the preparation of copper films by the CVD method.[270, 271] High evaporator temperatures are required in this case; in addition, the problem of film purity arises owing to the low volatility of the starting compounds.[111] Copper(I) halides are more volatile than copper(II) halides.[272 – 274] For example, dense fine-grain copper films with SER of 1.9 μΩ cm devoid of iodine admixture were obtained from CuI (the temperature of the SiO_2 substrate was 697 °C).[274] However, too high substrate temperatures are required for CVD process based on monovalent copper halides; this limits essentially the use of these compounds.

1. Copper(I) β-diketonates and their complexes

Among volatile copper(I) compounds, as among copper(II) derivatives, β-diketonates are promising for CVD technology. These compounds are attractive due to their ability to undergo disproportionation at comparatively low temperatures to give the corresponding volatile copper(II) β-diketonates and metallic copper directly in the form of thin films

$$2Cu^{I}(\beta\text{-diket}) \longrightarrow Cu^{0} + Cu^{II}(\beta\text{-diket})_2.$$

However, the operation with copper(I) β-diketonates has specific difficulties. First, the contact of these compounds with atmospheric oxygen during synthesis results in their smooth oxidation to the corresponding copper(II) β-diketonates, which necessitates that their synthesis be carried out in an inert atmosphere. Moreover, pure copper(I) β-diketonates are unstable and undergo disproportionation even at relatively low temperatures.[275] This can be prevented by additional complexing of the coordination-unsaturated copper atom with various ligands (Lewis bases).

Various organic and inorganic compounds (carbon monoxide, alkynes, dienes, phosphines, amines) forming volatile complexes (β-diket)$Cu \cdot L_n$ can be used as additional ligands. The additional ligand is eliminated upon disproportionation of the complex to give a volatile neutral compound

$$2(\beta\text{-diket})Cu^{I} \cdot L_n \longrightarrow Cu^{0} + Cu^{II}(\beta\text{-diket})_2 + 2n\,L\uparrow.$$

Of numerous compounds of this type synthesised to date, only compounds with H(HFA) satisfy the CVD process requirements. Derivatives of other β-diketones are generally insufficiently stable or do not provide reproducible results in the film synthesis. For example, rather stable complexes of Cu(acac) with trimethylsilylalkynes and trimethylsilylalkadiynes were obtained. These complexes were suggested as volatile CCC,[276] but CVD processes based on them have not been carried out.

We believe that the problem of stability of complexes with copper(I) β-diketonates, in particular with Cu(HFA), with additional ligands is a key problem for the evaluation of their possible use as the starting CCC in CVD technology. Thermodynamically stable complexes with high activation energies of thermolysis upon film deposition require high substrate temperatures or additional energy sources (plasma, laser radiation); this diminishes the advantages of these CCC over similar copper(II) β-diketonates which are much more readily accessible synthetically. Cu(I) complexes of low stability cannot provide the deposition efficiency and the process reproducibility. Hence, there should be a certain optimum degree of stabilisation of the Cu(HFA) molecule by virtue of the π-donor ability of a Lewis base used as the additional ligand. In fact, of all Cu(HFA)·L complexes synthesised, derivatives considered as potential starting CCC for CVD processes include those which contain moderately strong π-donors (*e.g.*, phosphines rather than amines) or compounds in which the π-donor ability of the multiple bond is somewhat weakened due to the incorporation of π-accepting trimethylsilyl groups [trimethylvinylsilane, bis(trimethylsilyl)acetylene].[277]

To date, several methods for the preparation of complexes of copper(I) β-diketonates with Lewis bases have been described. These include direct reaction with copper(I) oxide, the exchange reaction with sodium β-diketonates and metallation of β-diketones with monovalent copper compounds.[278–282]

$$Cu_2O + 2H(\beta\text{-diket}) + 2nL \longrightarrow 2(\beta\text{-diket})Cu \cdot L_n + H_2O, \quad (1)$$

$$ClCu \cdot L_n + Na(\beta\text{-diket}) \longrightarrow (\beta\text{-diket})Cu \cdot L_n + NaCl, \quad (2)$$

$$(\eta^5\text{-}C_5H_5)Cu \cdot P(CH_3)_3 + H(\beta\text{-diket}) \longrightarrow$$
$$\longrightarrow (\beta\text{-diket})Cu \cdot P(CH_3)_3 + C_5H_6. \quad (3)$$

Each of these variants involves certain synthetic difficulties. For example, reaction (1) is, technically, the simplest method.[282] However, water formed in the reaction favours undesirable disproportionation during the synthesis. In addition, it is difficult to monitor the stoichiometry of the products in this method.[283] The order of addition of the reagents is very important, since the formation of free Cu(I) β-diketonate, which undergoes disproportionation below 78 °C, should not be allowed. This is avoided by using an excess of the Lewis base.

The additional problem in method (2) involves the presence of sodium cations, which can appear as admixtures in the films obtained from the CCC synthesised using this approach.[111] The presence of these admixtures is absolutely unacceptable.

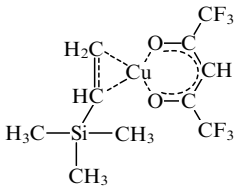
The reaction according to the pathway (3) occurs without complications; however, the cyclopentadienyl complex of copper(I) required is the least accessible potential starting compound of all three pathways.

a. Complexes of Cu(I) β-diketonates with alkenes and alkenylsilanes

The stabilising effect of the double bond in alkenes with respect to copper(I) β-diketonates is generally sufficient for the formation of stable complexes that can serve as the starting CCC. This is exemplified in the complex of (HFA)Cu(I) with vinylcyclohexane (VCH) synthesised[284] according to the procedure described previously.[282] Unfortunately, data on the physicochemical properties of this compound were not reported. The substrate temperature during the film deposition was 100–175 °C, which is lower than the temperatures for other CCC. The copper films obtained had low SER and virtually did not contain admixtures.

Of copper(I) derivatives stabilised by double bonds of the additional ligand, complexes of Cu(HFA) with alkenyltrimethylsilanes are among the most promising compounds for the synthesis of copper films.

It is known that the trimethylsilyl group manifests a significant π-acceptor effect[277] which is unfavourable for the coordination of the adjacent C=C bond of the alkene with the monovalent copper ion. In fact, the compound Cu(HFA) with the simplest alkenyltrimethylsilane, *viz.*, vinyltrimethylsilane (VTMS) **2** first described in 1991,[285] is readily oxidised in air to give copper(II) derivatives and is quickly decomposed at ~ 150 °C.[286]



2

The decomposition of (HFA)Cu(VTMS) was noted even on storage of this compound at room temperature.[287] However, these drawbacks are compensated by the fact that this compound is a volatile liquid even at 20 °C. The vapour pressure of (HFA).Cu(VTMS) is 0.14 Torr at 30 °C (see Ref. 288) and 0.3 Torr at 40 °C (see Ref. 289) and is considerably higher than the similar parameter for $Cu(HFA)_2$ up to 95 °C.[285]

The thermolysis activation energies of (HFA)Cu(VTMS) for various deposition conditions and substrate materials have been reported.[290,291] Various aspects of substrate surface pretreatment for maximising the deposition efficiency of copper films from this compound were studied in detail for TiN.[292–296] The best characteristics of copper films obtained from vapour on this widespread material were achieved on substrate surfaces pretreated with WF_6 vapour.[295]

On the whole, the CVD process involving (HFA)Cu(VTMS) has been studied rather thoroughly. An inert gas (He, Ar, N_2) or its mixture with H_2 was used as a carrier gas in most cases. It was shown[288] that the deposition rate of copper films increases with increase in the partial pressure of CCC vapour, reaching a maximum (36 nm min^{-1}) at a pressure of 5.7 mTorr. The SER of the copper films was ~ 2.2 μΩ cm at thicknesses > 500 nm. Similar values were obtained under the same or similar conditions in other studies.[297,298]

As mentioned above, the presence of a reducing gas (H_2) in the thermolytic disproportionation of copper(I) derivatives is generally unnecessary. Nevertheless, it was noted [296] that the characteristics of copper films can be improved essentially by additional annealing at 450 °C in a stream of Ar/H_2 (9 : 1). This increases the grain size in the films, and their SER is decreased from 2.35 to 2.12 μΩ cm.

Various aspects of the favourable effect of hydrogen as the carrier gas in the CVD process based on (HFA)Cu(VTMS) were considered by Lin and Chen.[299] It was shown that the use of H_2 provides denser copper films with lower SER values and increases the deposition rate. The film deposition rate can be increased additionally by substrate surface pretreatment with nitrogen plasma.

Braeckelmann *et al.*[300] studied the effect of the TiN substrate temperature in the range from 165 to 205 °C on the characteristics of copper films obtained from (HFA)Cu(VTMS) vapour. It was shown in particular that an increase in temperature decreased the SER of copper films from 2.15 to 1.8 μΩ cm and increased the deposition rate by a factor of 2.5. This is attributed to an increase in the CCC disproportionation rate. However, it was shown in a study of a similar process on W/Si substrates [301] that the SER of the copper films obtained in the substrate temperature range from 160 to 190 °C remained virtually unchanged. The temperature of 190 °C was found to be the optimum providing the maximum film growth rate (up to 500 nm min^{-1}).

It was found in a study of the deposition of copper films on a TiN substrate from (HFA)Cu(VTMS) vapour in a wider temperature range (from 160 to 330 °C) [290] that below 200 °C the SER of the films is ~ 2.0 μΩ cm. An increase in the temperature sharply impairs the morphology of the films and increases their SER.

In addition to the substrate temperature, the partial pressure of the starting CCC vapour is an important factor determining the deposition rate and the resulting copper film parameters. A study of the deposition of copper films from (HFA)Cu(VTMS) vapour (TiN/Ti/Si substrate at a temperature of 170 °C) at an overall pressure of 0.5 Torr showed [302, 303] that under these conditions, an increase in the partial pressure of CCC vapour to 0.048 Torr increased the deposition rate monotonically up to 25 nm min^{-1}, and the SER of the film decreased monotonically to 2.00 μΩ cm. With an increase in the partial pressure, the copper films became denser and had fewer surface defects. At partial pressures of (HFA)Cu(VTMS) vapour above 0.048 Torr, the deposition rate and the SER of copper films became virtually constant.

A similar dependence was obtained by Awaya and Arita.[304] It was shown that at temperatures below 200 °C, the rate of deposition of copper films from (HFA)Cu(VTMS) vapour is proportional to the square root of the CCC vapour partial pressure.

It was noted above that if copper(II) derivatives [for example, $Cu(HFA)_2$] are used in CVD process, the addition of water vapour to the carrier gas increased the growth rate of copper films while their SER remained unchanged, and in some cases (not always) also increased the process selectivity.[171, 190, 205, 225, 226] Similar effects were reported for (HFA)Cu(VTMS).

Deposition of copper films from (HFA)Cu(VTMS) vapour on SiO_2 and Pt/SiO_2 substrates at 150–250 °C gave copper films 800 nm thick with low SER in the absence of water vapour.[305] The addition of water vapour did not accelerate the process in the case of the SiO_2 substrate. In the case of Pt/SiO_2 substrates, a small increase in the deposition rate was observed, but much smaller than that with the use of copper(II) derivatives under the same conditions. The copper films obtained in the presence of water vapour had rough surface structure and high SER (> 20 μΩ cm).

More successful experiments on the deposition of copper films from (HFA)Cu(VTMS) vapour in the presence of water were carried out by Gelatos *et al.*[289] It was shown that at rather low partial pressure of water vapour (< 0.4 Torr), as in the case of $Cu(HFA)_2$ vapour, a sharp increase in the copper film deposition rate was in fact observed. This effect was particularly well pronounced at P_{H_2O} < 0.2 Torr. The specific electric resistance of the films obtained was 2.3±0.1 μΩ cm. Subsequent annealing decreased the SER to 1.9±0.1 μΩ cm, and the copper films had a considerably higher density than similar films obtained by CVD from (HFA)Cu(VTMS) vapour in the absence of water vapour. It was noted that such a low SER value was reached in the presence of water vapour at a film thickness of 50 nm, while under 'anhydrous' deposition conditions, this required a film thickness of at least 300 nm. An increase in the water vapour partial pressure to 0.75 Torr impairs strongly the characteristics of the films.[289, 306]

The possibility of optimisation of a CVD process involving (HFA)Cu(VTMS) and water vapour was studied.[307, 308] An important fact was noted: the preparation of copper films with low SER, good adhesion and high deposition rate requires that the injection of water vapour be carried out quickly in the beginning of the process. Copper films with SER of 1.9 μΩ cm (after annealing), and copper strips 0.4 μm wide and 1 μm thick with good characteristics were obtained under these conditions.

The addition of small amounts of H(HFA) vapour in the CVD of copper films from (HFA)Cu(VTMS) vapour can improve substantially the copper film morphology.[229] The presence of the β-diketone favours an accelerated and uniform growth of nucleation centres on the entire film surface, thus protecting it from cracks and roughening. However, the process loses its selectivity completely in this case.

One more variant for the deposition of copper films by the CVD method from (HFA)Cu(VTMS) vapour involves the addition of an excess of liquid VTMS to the starting CCC (40% – 60% relative to the volume of the starting CCC) before the evaporation.[309, 310] This enabled deposition rates of 40 – 60 nm min^{-1} to be achieved. It was noted that replacement of the carrier gas by hydrogen did not change essentially the film growth rate.[310] The mean specific electric resistance of the copper films obtained, with thicknesses from 200 to 1800 nm, was 1.86 μΩ cm; additional annealing of copper films at 600 °C in a high vacuum (10^{-7} Torr) decreased it to 1.76 – 1.77 μΩ cm.[309]

Simultaneous use of H(HFA) and VTMS vapour is possible.[311] The H(HFA) vapour increases the copper film deposition rate, and the VTMS vapour accelerates the CCC evaporation.

The rate of copper film deposition increases considerably if a CVD process with the use of (HFA)Cu(VTMS) vapour is carried out with simultaneous application of a shifting voltage of −30 V to the substrate.[312, 313] This effect is explained by reorientation of the dipole molecules of the starting CCC in the electric field stimulating their adhesion to the substrate.

The decomposition of (HFA)Cu(VTMS) vapour can be additionally promoted [as in the case of copper(II) derivatives as the starting CCC] by radiation. This variant can primarily be used in the preparation of microstructures from this CCC by lithographic methods.

In the study of Ochiani *et al.*,[314] deposition of copper films from (HFA)Cu(VTMS) vapour was carried out simultaneously with electron lithography. The copper film samples obtained had rather low SER.

The formation of copper films from (HFA)Cu(VTMS) exposed to an electron beam has been studied.[315] It was found that the energy threshold where decomposition starts is 4±0.5 eV and that decomposition occurs by dissociative electron addition. However, the films obtained by this method are considerably contaminated with carbon, apparently due to decomposition of HFA fragments under these rather drastic conditions.

A study of the preparation of thin copper strips 3 μm wide by thermal decomposition of (HFA)Cu(VTMS) vapour under argon laser radiation [286] showed that in this case, as with $Cu(HFA)_2$ vapour,[225] the addition of water vapour to the vapour of the starting CCC affects favourably the deposition rate and the characteristics of the resulting copper microstructures. The SER values of the best copper strips obtained this way were close to the SER of metallic copper. Similar results were obtained under

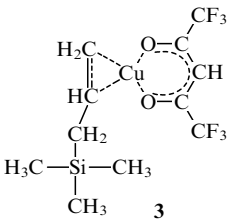
analogous conditions;[316] it was also noted that the morphology of the surface copper strips depends essentially on the laser radiation power. Moilanen *et al.*[317] achieved rather high film deposition rates of up to 400 nm s^{-1}, but the SER of the strips increased somewhat (up to 3.7 μΩ cm).

Thin copper strips (channels) up to 16 μm deep were obtained by CVD using decomposition of (HFA)Cu(VTMS) vapour.[318] The specific electric resistance of the copper channels was 1.95 μΩ cm; annealing gave a value of 1.86 μΩ cm.

Successful optimisation of preparation of copper strips with SER of $\leqslant$ 2.0 μΩ cm using CVD from (HFA)Cu(VTMS) vapour was reported.[319]

Popovici *et al.*[320] observed the terrace growth of copper films during the decomposition of (HFA)Cu(VTMS) vapour on Teflon substrates under excimer laser radiation (λ = 248 nm). It was assumed that growth of this type occurs owing to the interference between the Teflon support and the precipitated copper layers.

In turn, the successful use of (HFA)Cu(VTMS) vapour as a convenient starting CCC for the CVD process has served as an incentive for the search for volatile Cu(HFA) complexes with similar compositions and physicochemical characteristics. As a result, new starting CCC were reported, where allyltrimethylsilane (ATMS) (for example, compound **3**)[321–323] and vinylalkoxysilanes, such as vinyltrimethoxysilane (VTMOS),[287] vinyl(dimethoxy)methylsilane (VDMOMS)[324] and vinyltriethoxysilane (VTEOS),[324, 325] served as Lewis bases. These CCC are more stable than (HFA)Cu(VTMS). They are liquid at room temperature, but data on their physicochemical properties were not reported in these studies.



3

If (HFA)Cu(VTMOS) vapour is used, the optimum temperature range for the TiN substrate, where copper films with the best characteristics are formed, is 175–200 °C.[287] The lowest SER of the films obtained under these conditions is 2.5 μΩ cm.

Somewhat better results (deposition rate up to 100 nm min^{-1} and lower SER of the films) were obtained in CVD processes based on (HFA)Cu(VDMOMS) and (HFA)Cu(VTEOS).[324, 325] It was noted that the presence of water vapour during the deposition of films is necessary for the former compound.[324]

Very interesting results were obtained in CVD processes using (HFA)Cu(ATMS). It was found that, other conditions being equal, the incorporation of ATMS in the complex decreases considerably the temperatures for copper film deposition in comparison with those for similar compounds without ATMS. (HFA)Cu(ATMS) evaporates well at 40–45 °C and forms copper films with low SER at substrate temperatures of 60–170 °C.[321] It was noted that the film parameters remain almost unchanged in this rather wide temperature range. A certain role in these features of CVD processes is apparently associated with the fact that (HFA)Cu(ATMS) is even less stable thermally than (HFA)Cu(VTMS) and (HFA)Cu(VTMOS), and hence it is more reactive.[323, 326] At a temperature as low as 60 °C, the IR spectra of (HFA)Cu(ATMS) vapour contain bands corresponding to $Cu(HFA)_2$. It is interesting that the morphology of the copper film surfaces obtained also depends on the reactivity of the starting compounds: for example, the grain size in the copper films obtained from (HFA)Cu(ATMS) vapour is much larger than that in the copper films obtained from (HFA)Cu(VTMS) vapour.[323]

b. Complexes of copper(I) β-diketonates with isocyanides

Of copper(I) β-diketonate complexes stabilised by interactions of the copper(I) ion with the double bond, those with *tert*-butyl isocyanide (Bu^tNC) are considered as promising starting CCC for the preparation of copper films by CVD technology. It should be noted that the corresponding complexes of copper(I) derivatives with nitriles RCN decompose even at room temperature.[327] It is known that the nitrile group is an efficient π-acceptor [the resonance constant is $\sigma_R^0 = +0.08$ (see Ref. 277)] and hence it cannot form stable complexes with the copper(I) ion. On the other hand, the corresponding effect of the isocyanide group is close to zero,[277] and the additional π-donor *tert*-butyl group makes the complex sufficiently stable.

Kruck and Terfloth[328] reported data on the synthesis [by method (2)] and the physicochemical properties of volatile $(HFA)Cu \cdot Bu^tNC$ and $(HFA)Cu \cdot (Bu^tNC)_2$ complexes (in particular, the sublimation temperatures at 0.1 Torr are 55 and 95 °C, respectively). CVD processes with the use of vapour of these compounds gave copper films with good characteristics.[329]

c. Complexes of copper(I) β-diketonates with dienes

Dienes form rather stable 1 : 1 complexes with the copper(I) ion. Copper(I) β-diketonates are usually stabilised by 1,5-cyclooctadiene (1,5-COD).

Like complexes with VTMS, complexes of 1,5-COD with Cu(acac) and Cu(TFA) have low stability;[282] on the contrary, (HFA)Cu(1,5-COD) is a very stable compound which sublimes without decomposition at 65–70 °C and remains unchanged in air for a period of one year. The vapour pressure of this compound is ~ 56 mTorr at 62 °C.[330]

The spatial structure of the (HFA)Cu(1,5-COD) molecule (Fig. 3) was determined[282] and analysed in detail.[280] It was noted in the latter study that the actual coordination of the Cu(I) centre is more complex than Fig. 3 shows and fits a 3 + 1 scheme. In other words, the 1,5-COD fragment is coordinated asymmetrically. Decomposition of vapour of this CCC at 200 °C resulted in copper film formation and evolution of volatile decomposition products, *viz.*, $Cu(HFA)_2$ and 1,5-COD.[282]

The preparation of copper films by CVD from (HFA)Cu(1,5-COD) vapour has been described in a number of papers.[330–335] For example, it was noted[330] that a temperature of 65 °C in the evaporator and a temperature of 70 °C of the reactor cell walls are sufficient for the process. Admixtures of carbon, oxygen and fluorine are virtually absent in the films (< 1%).

The specific electric resistance of films obtained from (HFA)Cu(1,5-COD) vapour depends primarily on the substrate temperature. At the optimum temperature (190–210 °C), the SER of the films was 1.97±0.10 μΩ cm. Higher deposition rates (> 15 nm min^{-1}) and larger film thicknesses (> 250 nm) worsen this parameter.

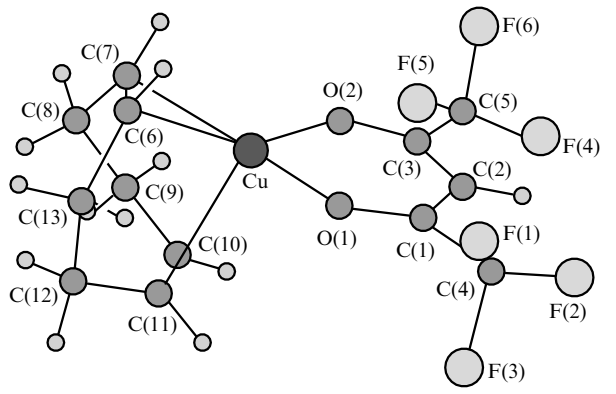


Figure 3. (HFA)Cu(1,5-COD) molecule.

(HFA)Cu(1,5-COD) is a promising starting compound in an aerosol modification of CVD technology.[335] The films are deposited from an aerosol of a toluene solution of the starting compound. The aerosol is fed to the reactor cell in a stream of an inert gas (nitrogen); intermediate preheating of the vapour to 40–100 °C is provided. Even at a substrate temperature of 120 °C, crystalline copper films were obtained; their SER were within 1.7–3.5 μΩ cm under optimum process conditions (140 °C, deposition rate 80 nm min^{-1}).

Copper films with good characteristics are obtained using (HFA)Cu(1,5-COD) as the starting CCC in the presence of CO.[336] Carbon monoxide displaces the 1,5-COD ligand from the complex at −70 °C to give an intermediate unstable carbonyl compound, (HFA)Cu(CO), which in this case serves as the starting CCC in the CVD process. Isolation of this carbonyl complex in a pure state failed.

1,5-COD is not the only diene that can give volatile complexes with copper(I) β-diketonates applicable in CVD technology. In particular, a hydrocarbon which is rare but quite accessible synthetically, *viz*., 7-*tert*-butoxynorbornadiene 7-Bu^{t}O-NBD, was suggested for this purpose[337] (for its synthesis, see Ref. 338). Using a procedure which is a modification of the method (2), Chi *et al*.[337] obtained a series of complexes of the type (β-diket)Cu(7-Bu^{t}O-NBD), where β-diket = acac, TFA, HFA, FOD, with sublimation temperatures from 75 to 90 °C at 0.1 Torr. The geometry of the molecules was determined for all of these complexes. However, only one of these compounds, namely, Cu(HFA)(7-Bu^{t}O-NBD), was found to be suitable for the preparation of copper films. The specific electric resistance of the films was satisfactory at sufficiently high substrate temperatures; the SER of films increased abruptly (> 1000 μΩ cm) and their surface morphology is deteriorated upon decrease in the temperature of the substrate to 170 °C.[337]

d. Complexes of copper(I) β-diketonates with alkynes

It is known that the triple bond, particularly that in alkyl-substituted acetylenes, has a stronger π-donor effect than the double bond.[277] Hence, alkynes should form sufficiently stable complexes with the copper(I) atom in β-diketonate derivatives.

The first synthesis of volatile η^2-complexes of Cu(HFA) with alkynes, *viz*., but-2-yne, bis(trimethylsilyl)acetylene and diphenylacetylene, was carried out by the reaction of (HFA)Na with CuCl in the presence of excess alkyne.[278] Volatile Cu(HFA) complexes with pent-2-yne[339] and hex-3-yne[340] were also obtained. A little later, a simple one-stage procedure was proposed for the synthesis of Cu(HFA) complexes with but-2-yne[341] and bis(trimethylsilyl)acetylene.[342] A series of compounds of this class containing silicon atoms at the triple bond were patented as the starting CCC for CVD technology.[343]

According to X-ray diffraction data, the copper(I) atom in the compounds in question has a flat trigonal configuration with coplanar diketonate and alkyne ligands (Fig. 4).[278] The nature of bonding and the electron interaction of the fragments in this type of complex was studied in more detail using ^1H and ^{13}C NMR spectroscopy.[281, 342]

The possibility of the existence of equilibrium between mononuclear and binuclear forms of these complexes was also considered,[342] as some of them undergo chemical transformations in the bubbler of the CVD reactor at 45–65 °C to give low-volatility products.[340, 341] In this case, the corresponding binuclear complexes are obviously formed by μ-η^2 bonding of the triple bond with the copper atom [the ratio alkyne : Cu(HFA) = 1 : 2]. Such complexes are also known in the chemistry of other transition metals.[344, 345] However, in this case the complexes are extremely unstable[342] and can only be formed as labile intermediates. On the whole, the nature of this reaction has been studied insufficiently.

The Cu(HFA) complex with but-2-yne is decomposed on the substrate at 150–210 °C under the conditions of the CVD process to give dense mirror-like copper films with low SER.[339] The rate of deposition of such films can be increased by addition of water vapour.[306] The possibility of selective deposition of copper films starting from this compound was considered.[346]

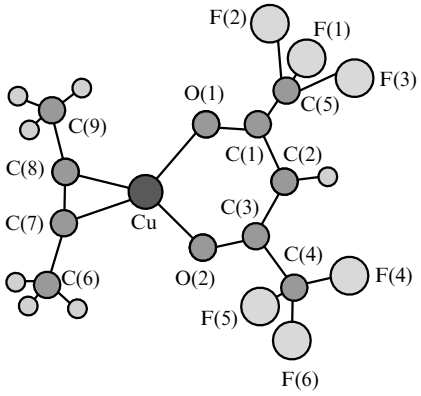


Figure 4. (HFA)Cu($CH_3C{\equiv}CCH_3$) molecule.

An unusual modification of this type of the starting CCC was suggested by Schmidt and Behrens.[347] They synthesised a volatile 2 : 1 Cu(HFA) complex with bis(*tert*-butylethynyl) sulfide. It was shown that the sulfur atom did not participate in coordination with the copper(I) ion. Similar Cu(I) complexes with other β-diketonates as the ligands were found to be unstable even at room temperature.

e. Complexes of copper(I) β-diketonates with phosphines

Yet another possibility to stabilise Cu(HFA) is the preparation of its complexes with derivatives of VA Group elements. Of these derivatives, trialkylphosphines are used most widely as additional ligands. However, the volatility of biscomplexes of the type (β-diket)Cu($PAlk_3$)$_2$ synthesised first[348] was insufficient for their use in CVD technology.

The syntheses of volatile monomeric 1 : 1 complexes of copper(I) β-diketonates with organic phosphines for CVD were first reported by Shin *et al*.[349–351] Initially, the reaction according to pathway (3) became the main method for their synthesis;[351] the applicability of pathway (2) was shown later.[279, 352] The compounds obtained were low-melting crystals capable of sublimation or viscous liquids.

As in the case of similar complexes with 1,5-COD,[280] the HFA derivative (Fig. 5) was the most stable of the series of compounds with the general formula (β-diket)Cu(PMe_3), where β-diket = acac, TFA, HFA.

The same is true for complexes with other trialkylphosphines.[352] To interpret this phenomenon and to study the nature of the interaction of the copper(I) ion with the phosphine molecule, photoelectron spectroscopic data and quantum-chemical calculations were used.[353]

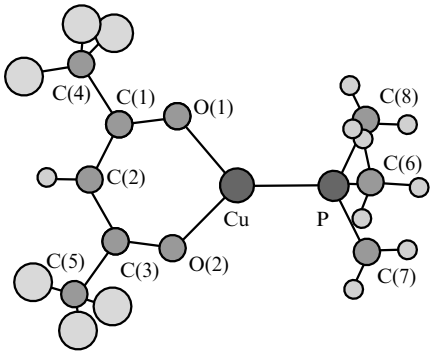


Figure 5. (HFA)Cu(PMe_3) molecule.

The vapour pressure of Cu(HFA)(PMe_3) was measured at various temperatures and the $\log P - 1/T$ relationship was plotted.[279] The corresponding vapour pressures of Cu(HFA)(PMe_3) and $Cu(HFA)_2$ were found to be similar.[179]

The first experiments on CVD of thin films with the use of phosphine complexes of copper(II) β-diketonates as CCC gave promising results. For example, a rather high deposition rate (up to 100 nm min^{-1}) was achieved at 150 °C on a Pt/SiO_2 substrate resulting in dense mirror-like copper films with good adhesion.[354] It was reported that the process can occur selectively.[350] A more detailed study showed that phosphine complexes of Cu(HFA) have higher selectivity than similar complexes with 1,5-COD or alkynes under comparable conditions.

Thin copper films were also deposited from Cu(HFA)(PMe_3) vapour in the presence of water and organic solvents (alcohols, toluene, tetrahydrofuran).[206] It was shown that this compound can react with water at room temperature with partial oxidation of copper(I) to copper(II). The use of alcohols results in reversible coordination of the alcohol molecules with copper(I) ions with formation of a more volatile alkoxide and, hence, leads to an increase in the deposition rate of copper films.

2. Volatile compounds of copper(I) devoid of β-diketonate ligands

A series of volatile derivatives of monovalent copper includes CCC which are not inferior to β-diketonates in terms of physicochemical properties required in CVD technology. Such CCC can be considered as alternatives to the classical β-diketonate copper(I) complexes. An obvious direction of the molecular design of such compounds is some structural similarity to copper β-diketonates. In view of this, we included copper β-iminoketonates and β-oxocarboxylates in our consideration.

Yet another direction in the creation of new CCC is the search for fragments capable of replacing completely the β-diketonate group while preserving the properties needed for CVD technology. The promising compounds of this type include alkoxides, amides, cyclopentadiene derivatives and heterocyclic compounds (*e.g.*, pyrazole derivatives).

a. Copper(I) β-iminoketonates and β-oxoacid derivatives

Fluorinated β-iminoketones required for the synthesis of stable nitrogen-containing analogues of copper(I) β-diketonates are obtained by a two-step procedure from the corresponding β-diketones.[355] This fact itself implies the low competitiveness of copper(I) β-iminoketonates synthesised from sodium β-iminoketones by reaction (2) in comparison with similar copper(I) β-diketonates.

At room temperature, complexes of this series (with trialkylphosphines as additional ligands) are volatile liquids or solid compounds. A study of whether copper films can be obtained by CVD from vapours of copper(I) β-iminoketonates did not reveal any considerable advantages of these compounds over the more accessible oxygen analogues,[355, 356] *i.e.*, copper(I) β-diketonates. Only one study was published[357] reporting good results in the preparation of copper films by CVD with the use of a complex of copper(I) 3-oxobutanoate with trimethylphosphine which is rather stable and resistant against oxidation in air.

b. Copper(I) alkoxides

The main drawback of copper(I) alkoxides as potential CCC for CVD technology is their rather easy transition into non-volatile polymers. Nevertheless, successful attempts at the preparation of copper films from tetrameric copper(I) *tert*-butoxide $[Cu(OBu^t)]_4$ were reported.[358, 359] The pyrolysis temperature of this compound is rather high (~ 400 °C). As indicated by Lemmen *et al.*,[360] this compound is rather sensitive to oxygen and atmospheric moisture (the films obtained contained from 2% to 5% of oxygen), therefore it was not widely used in CVD technology.

Hampden-Smith *et al.*[361] synthesised a volatile monomeric complex of copper(I) *tert*-butoxide with trimethylphosphine (Bu^tO)Cu(PMe_3). The CVD method made it possible to obtain pure copper films containing no oxygen and phosphorus admixtures from this compound.[361]

c. Amide derivatives of copper(I)

In the series of volatile amide derivatives of copper(I), there is one unusual compound used as a CCC, *viz.*, the tetrameric cluster $\{Cu[N(SiMe_3)_2]\}_4$.[362] This compound sublimes at rather high temperature (~ 180 °C). Nevertheless, it produces copper films with satisfactory characteristics. It is possible that further research on copper(I) amide derivatives will allow one to obtain compounds of this class that would be more volatile and, accordingly, more promising for CVD technology.

d. Cyclopentadienyl derivatives of copper(I)

Cyclopentadienyl derivatives of copper(I) compete satisfactorily with copper β-diketonates as starting compounds in CVD processes. Cyclopentadienyl derivatives of copper(I) are usually stabilised by trialkylphosphines and isocyanides.

Trialkylphosphine complexes of cyclopentadienylcopper(I) are usually synthesised using a procedure similar to the pathway (2) from cyclopentadienylsodium and halophosphine complexes of copper(I).[363, 364] Their typical sublimation temperatures are 60–70 °C, and the thermal decomposition temperatures are 120–125 °C.[365] The calculated vapour pressure of (Cp)Cu(PMe_3) at 80 and 100 °C are 14 and 30 Torr, respectively.[7]

For similar platinum compounds, it was found that incorporation of a methyl group in the cyclopentadiene ring increases considerably the volatility of the compound.[364] In view of this, copper(I) methylcyclopentadienyl complexes with trialkylphosphines were synthesised,[363] but their sublimation temperatures and vapour pressures were almost the same as those of the non-substituted analogues. A study of the physicochemical properties showed that the methyl-substituted derivatives are less stable and undergo decomposition at temperatures 15–20 °C lower than the non-substituted compounds. This is an advantage of methyl-substituted cyclopentadienyl derivatives of copper(I) for the CVD process. Recently, a number of methyl- and ethyl-substituted cyclopentadienyl complexes of copper(I) with triisopropylphosphine were patented as promising volatile CCC for CVD technology.[366]

Originally, such complexes were used in CVD for the synthesis of mixed copper-containing semiconductor systems of the $CuGaS_2$ type.[365] The first studies on the CVD of copper films with the use of these complexes gave good results. For example, it was shown[367] that decomposition of (Cp)Cu($PAlk_3$) vapour (Alk = Me, Et, Bu) on substrates made of different materials *in vacuo* gave high-purity copper films with a SER that differed from the SER of bulk metallic copper by ~ 10%. Based on (Cp)Cu(PMe_3), copper films with SER of 1.8–2.2 μΩ cm were obtained,[361] but this value was achieved only after annealing. The morphology of the surface of copper films formed from (Cp)Cu(PEt_3) vapour on SiO_2 was considered in detail.[368]

The (Cp)Cu(PEt_3) complex was used as the starting CCC in laser-activated preparation of copper strips and in thermal laser lithography.[369] Irradiation of a thin layer of this compound with the light of an argon laser at $\lambda = 514$ nm gave a copper strip containing less than 10% carbon and with SER of ~ 6.8 μΩ cm. The use of radiation excimer lasers with shorter wavelengths resulted in strips of copper–carbon composites.

The (Cp)Cu(PEt_3) complex was used for the CVD synthesis of thin copper–aluminium films *in situ*.[7] In this method, the rather low concentration of copper (~ 1.4%) decreases greatly the SER of the basic aluminium film. The valuable property of (Cp)Cu(PEt_3) is that, unlike the majority of the starting volatile CCC, it is chemically inert with respect to the second aluminium-containing starting compound used simultaneously, *viz.*, dimethylalane $(CH_3)_2AlH$.

As in the case of Cu(HFA), *tert*-butyl isocyanide can be used for the stabilisation of copper(I) cyclopentadienyl complexes. The

(Cp)Cu(Bu^{t}NC) compound was obtained for the first time using method (1) and was used as a catalyst of some organic reactions.[370] Later, this substance was synthesised using method (2) and was suggested as a starting CCC for the preparation of copper films by CVD.[328] Studies of the behaviour of this compound in CVD showed[329, 371] that high-quality films free from carbon admixtures can in fact be obtained on its basis. The optimum substrate temperature range is 200–350 °C,[371] although noticeable decomposition of (Cp)Cu(Bu^{t}NC) starts at 135 °C.[328]

e. Complexes of copper(I) with pyrazole derivatives

Many volatile compounds are known in which the copper(I) ion is bound to heterocyclic fragments. However, only one study is devoted to the synthesis of copper(I) pyrazolyl borate complexes with triethylphosphine.[372] At a substrate temperature of 150 °C, these compounds give polycrystalline copper films with good characteristics and high selectivity. Apparently, studies in this direction will continue.

3. Mechanisms of decomposition of copper(I) derivatives on the substrate

It is generally believed that copper films are formed from monovalent copper–HFA complexes due to their disproportionation followed by removal of the volatile product. The formation of $Cu(HFA)_2$ from (HFA)Cu(VTMS) in the gas phase was proved by spectral methods.[189, 373]

The initial step of (HFA)Cu(VTMS) decomposition should apparently involve cleavage of the weakest bond in the molecule, *i.e.*, the bond between the copper(I) ion and the VTMS molecule. The question is, where does this cleavage occur? There are two answers to this question: first, on the substrate surface; second, in the vapour phase. Evidence in favour of both variants can be found in the literature.

The majority of the authors favour the first variant.[201, 290, 374] For example, a comparative study of the $Cu(HFA)_2$ and (HFA)-Cu(VTMS) decomposition by Fourier IR spectroscopy revealed bands unambiguously assigned to the VTMS ligand in the spectra of (HFA)Cu(VTMS) adsorbed on a Si(100) substrate at −148 °C.[201] However, these bands disappeared at 27 °C, which made it possible to conclude[201] that at this temperature VTMS was eliminated extremely quickly from the adsorbed compound. The disproportionation of the resulting Cu(HFA) molecules was proved and considered in detail.[310, 374–376]

Thus, taking this into account, one can make the conclusion that the most probable mechanism of decomposition of (HFA)Cu(VTMS) vapour involves four steps:

(1) adsorption of the entire molecule on the substrate

$$(HFA)Cu(VTMS)_{(vapour)} \longrightarrow (HFA)Cu(VTMS)_{(ads)};$$

(2) elimination of VTMS followed by fast desorption

$$(HFA)Cu(VTMS)_{(ads)} \longrightarrow (HFA)Cu_{(ads)} + VTMS\uparrow;$$

(3) bimolecular disproportionation of the intermediate formed

$$2(HFA)Cu_{(ads)} \longrightarrow Cu_{(ads)} + Cu(HFA)_{2(ads)};$$

(4) desorption of the volatile product of $Cu(HFA)_2$ disproportionation

$$Cu(HFA)_{2(ads)} \longrightarrow Cu(HFA)_{2(vapour)}\uparrow.$$

However, studies of the kinetics of (HFA)Cu(VTMS) decomposition[377] gave evidence in favour of the second variant, *i.e.*, molecular decomposition in the vapour phase. Hence, it is the intermediate Cu(HFA) that should be considered the actual starting compound in the copper film formation. The second mechanism, alternative to the one mentioned above, is as follows:

(1) vapour-phase thermolysis

$$(HFA)Cu(VTMS)_{(vapour)} \longrightarrow (HFA)Cu_{(vapour)} + VTMS\uparrow;$$

(2) adsorption of the intermediate

$$(HFA)Cu_{(vapour)} \longrightarrow (HFA)Cu_{(ads)};$$

(3) bimolecular disproportionation of the intermediate formed

$$2(HFA)Cu_{(ads)} \longrightarrow Cu_{(ads)} + Cu(HFA)_{2(ads)};$$

(4) desorption of the volatile product of $Cu(HFA)_2$ disproportionation

$$Cu(HFA)_{2(ads)} \longrightarrow Cu(HFA)_{2(vapour)}\uparrow.$$

The third and fourth steps are similar in both cases.

It is possible that bimolecular disproportionation (third step) is not the only pathway for the transformation of the Cu(HFA) intermediate. A direct relationship between the activation energy of the copper nucleation from (HFA)Cu(VTMS) on the surface and the electric conductivity of the substrate was established; this is believed[378] to suggest a certain role of one-electron transfer from the surface to the adsorbed Cu(HFA), which was not taken into account in the mechanism considered above.

One can imagine a situation (for example, at a sufficiently high temperature of the vapour flow) where a portion of molecules of the starting CCC are decomposed in the vapour phase, while the other portion do so on the substrate surface. The relative fractions of each process depend on the particular conditions of the process.

The effect of the substrate temperature on the mechanism of low-vacuum deposition of the copper film from the (HFA)Cu(VTMS) vapour was studied in detail.[298] It was shown that in the temperature range of 140–220 °C, deposition obeys the Arrhenius law; at temperatures higher than 220 °C, the process switches to the saturation mode (the 'transport-limited' situation). In this mode, the SER of the film and the content of contaminating carbon increase.[379] In addition, the film formed becomes less uniform due to a decrease in mobility of copper atoms under the effect of the atoms of the quickly growing surface layers.[380]

The mechanism of the effect of partial pressure of (HFA)Cu(VTMS) vapour on the characteristics of films considered by Lee *et al.*[302] fits completely the deposition scheme described above. At low partial pressure of CCC vapour, the sites for the adsorption of the Cu(HFA) intermediates are preserved on the substrate surface. As the pressure is increased to a certain threshold, the surface becomes 'adsorption-saturated' and the copper film deposition rate no longer depends on the partial pressure.

As in a case of $Cu(HFA)_2$, a special situation arises if CVD is carried out with the use of (HFA)Cu(VTMS) under ultrahigh vacuum (10^{-9}–10^{-10} Torr).[199] Under these conditions, the first stage involves chemisorption of the entire CCC molecule on the substrate (TiN). At 27 °C, the CCC is completely transformed to the adsorbed Cu(HFA) intermediate, which does not disproportionate upon heating but is decomposed to CO, CO_2, CF_4 and metallic copper. About 90% of the copper contained in the precursor remains on the substrate [~ 30% in the case of $Cu(HFA)_2$ under the same conditions]. At 280 °C, the diffusion of copper into the substrate starts.

It is believed[306] that the favourable effect of water vapour on the deposition rate of copper films upon decomposition of (HFA)Cu(VTMS) vapour is associated with facilitation of the VTMS ligand elimination. The observed impairment of the characteristics of copper films at high partial pressure of water vapour[289, 306] occurs because of the side reaction of water with the adsorbed Cu(HFA) intermediate resulting in a Cu_2O admixture in the films. Experiments with water labelled with the ^{18}O isotope showed that it is the oxygen atoms from water molecules that are incorporated in the film.[306]

A mechanism of (HFA)Cu(VTMS) decomposition under ion beam impact to give copper films has been suggested.[381]

The decomposition mechanism of other copper(I) derivatives, such as Cu(HFA)(1,5-COD), and Cu(HFA) complexes with but-

2-yne on a silicon substrate during the CVD process (~ 210 °C) is totally similar to the mechanism considered above [375, 382] (including that in the presence of water vapour [306]). However, there are no data on the elimination of additional ligands (Lewis bases) from these compounds directly in the vapour phase.

The mechanisms of transformations in thin copper films during their subsequent annealing [289, 309] have not been elucidated so far. The available data on the effect of annealing on the characteristics of films are rather contradictory. For example, it was reported that annealing of films decreased their SER considerably,[289, 383] decreased it slightly [309] or did not affect it.[384] This could result from processes affecting the SER in opposite ways: annealing increases the film crystallinity and, on the other hand, favours their oxidation and enhances the diffusion of copper atoms into the substrate material.[385]

The mechanism of thermal decomposition of the vapour of copper(I) *tert*-butoxide tetramer on the substrate was studied in detail.[359] It was shown that a homolytic process results in intermediate *tert*-butyl radicals and copper(I) oxide; the effect of the latter can explain the presence of oxygen in the films obtained. On the other hand, thermal decomposition of a vapourised phosphine complex of copper(I) *tert*-butoxide did not result in either the formation of Cu_2O or an admixture of oxygen in the films. Data on the deposition conditions of copper films from copper(I) derivatives and the corresponding SER values are listed in Table 5.

Table 5. CVD conditions and properties of copper films obtained from copper(I) compounds.

Starting CCC	T /°C	P /Torr	Barrier layer	Substrate	T_p /°C	Carrier gas	SER /μΩ cm	Ref.
(HFA)Cu(VCH)	45 – 55		TiN	Si	100 – 175	Ar	1.9 – 2.3	284
(HFA)Cu(VTMS)	–		TiN	Si	200 – 250		1.9 – 2.3	289
	–		TiN	Si	165 – 205	H_2O	1.8 – 2.06	300
	–		W, SiO_2,	$CoSi_2$	160 – 300		–	291
	–		TiN	Si(100)	300	H_2O, H_2	–	260, 308
	–		–	Si		H(HFA), VTMS	1.8	311
	–	0.5	Si_3N_4	Si	220 – 250	VTMS, N_2	1.82 – 1.86	309, 310
	–		W, TiN,	Al	140		–	386
	–	0.12	TiN, TiW	SiO_2	200	Ar/N_2	3 – 10	387
			SiO_2	Pt, SiO_2		H_2O	> 20	305
	–		W,	SiO_2, Si		H_2O	2.0 – 12.0	306, 388
	–		TiN,	SiO_2, Si	< 200		2.0	290
	–		TiN	Si	150 – 200 [a]	N_2	1.8	389
	–	0.12	–	Si	150 – 200 [a]		3.6	314
	–		–	Si	150 – 200 [b]		–	316
	–		TiN	Si	150 – 200 [c]	H_2	–	206
	–		Si_3N_4, SiO_2	–	150 – 200 [b]		3.7	317
	50	2	TiN	Si	100 – 300	Ar	–	379
	–		TiN, Ti	Si	180		2.35	296
	40	0.5	TiN, TiW	Si	170	He	2.0	302
	–		–	SiO_2, Pt	225		–	378
	–		–	Si	150 – 250	H_2	–	390
	33	0.06	TiN, TiW	Si	130 – 180	H_2	2.2 – 2.3	288
	70 – 80	–	TiN	Si	120 – 180		–	377
	–		TiN	SiO_2	75 – 250		2.0	284
(HFA)Cu(ATMS)	40 – 45	–	TiN	Si(100)	60 – 170		1.7 – 1.9	321
	60 – 90	–	–	Si	275		2.0	322
(HFA)Cu(VDMOMS)	–	–	–	Si	195	H_2O	2.0	324
(HFA)Cu(VTEOS)	–		–	Si	195		2.0	324
	70 – 80		–	Si(100)	180 – 220	N_2	2.0	325
(HFA)Cu(VTMOS)	60 – 65	–	TiN	Si	175 – 200	Ar	2.5	287
	–		TiN	Si	160 – 220		–	351
(HFA)Cu(1,5-COD)	62	0.07	–	Si	190 – 210		1.97 ± 0.10	330
	–		Ag	Si(111)	180 – 300		2.0 – 2.4	334, 375
	–	760	SiO_2	Si, W	140	N_2	1.7 – 3.5	335
(HFA)Cu(7-Bu^{t}O-NBD)	–		–	Pt, SiO_2	> 200		< 6	337
(HFA)Cu($CH_3C{\equiv}CCH_3$)	–		SiO_2	Si	210		2.0	339
(Bu^{t}O)Cu(PMe_3)			Pt	SiO_2	260 – 450		10 – 12 (1.8 – 2.2) [e]	361
(Cp)Cu(PMe_3)	–		W, SiO_2	Si [d]	150 – 220		2.0	367
	–		–	Pt, SiO_2	260		1.8 – 2.2 [e]	361
(Cp)Cu(PEt_3)	–		W, SiO_2	Si	150 – 220		2.0	363, 367
	66	400	SiO_2	Si(100)	280 – 550	H_2	–	368
	–		SiO_2	Si	280 – 550 [b]		6.8	369
(Cp)Cu(PBu_3)	–		W, SiO_2	Si [d]	150 – 220		2.0	367
$[CuN(SiMe_3)_2]_4$	180	0.2	–	Si	145	H_2	–	362

[a] Under a 30 – 50 keV electron beam. [b] Under argon laser irradiation. [c] Under krypton laser irradiation. [d] Other supports were also used. [e] After annealing of the films at 600 °C.

VI. The problem of selective deposition of copper films

The selectivity of deposition of copper films by the CVD method from the vapour of copper(II) and copper(I) derivatives deserves a separate discussion. Let us note the short reviews [391, 392] on the subject.

The selectivity of deposition implies preferential growth of the copper film on the surface of a certain material relative to the surface of some other material. This problem is important because at the present time there are no versatile methods for etching copper films covering the entire surface of a sample, which would allow one to obtain predetermined shapes on the surface required in the production of microelectronic devices.

For example, a method for the dry etching of copper by consecutive treatment of its surface with H_2O_2 (which oxidises copper to Cu_2O) and H(HFA) (which transforms Cu_2O into a volatile copper β-diketonate) was suggested.[388] A similar idea was implemented by Steger and Masel [393] who used H(HFA) vapour in a stream of O_2. However, though high etching rates were achieved [~ 1000 nm min^{-1} at 190 °C (see Ref. 388) and ~ 1500 nm min^{-1} at 350 °C (see Ref. 393)], these techniques did not become popular. This is also true for the other known etching methods requiring rather drastic conditions, such as a method with the use of $SiCl_4$ in a stream of N_2 ($T > 250$ °C) [394] and treatment with a mixture of chlorine and PEt_3 vapour in the presence of H(HFA) at 420 – 540 °C.[395]

1. Deposition of copper films in 'metal – dielectric' systems

As a rule, SiO_2 is used as a dielectric for the deposition of copper films in 'metal – dielectric' systems.

The growth of a copper film on a dielectric substrate surface primarily depends on the ease of adsorption of molecules of volatile CCC and compounds accompanying the process on the surface. The growth step following adsorption is nucleation, *i.e.*, formation of primary grains of the growing film at the sites where adsorption is the most efficient and where decomposition of molecules of the CCC mostly starts. It was assumed that it is this step that determines the overall process selectivity.[387]

Hence, the simplest solution for the selectivity problem can involve suppressing the nucleation [396] or providing conditions where adsorption of molecules of the CCC on the dielectric surface is suppressed, while that on the metal surface is not suppressed. However, this solution also involves certain difficulties. The main of these results from the fact that, depending on the deposition conditions (temperature, pressure, carrier gas), the adsorption of molecules of CCC can be either physical or chemical.[203] Therefore, a versatile method for the treatment of SiO_2 substrate surfaces in order to minimise adsorption and achieve the maximum selectivity obviously cannot exist: everything depends on the particular CVD technology and the CCC used.

The nature of selectivity in the deposition of copper films from $Cu(HFA)_2$ vapour on Ag/SiO_2 substrates was considered in detail by Cohen *et al.*[376] It was assumed that selectivity is provided due to the existence of several paths of the CVD process: on the surface of silver, fast reduction of copper(II) to copper(I) occurs with desorption of the HFA ligand due to electron transfer from the metal surface, whereas on the surface of the SiO_2 dielectric, the molecules of the starting CCC are adsorbed in the original state.

The consecutive growth of film layers relative to the dielectric substrate can be regarded as a particular case of the above scheme. Deposition of copper films by decomposition of $Cu(HFA)_2$ vapour in the presence of water vapour decreases greatly the selectivity of film growth in comparison with the 'water-free' technique.[171, 205] On the other hand, the presence of water vapour increases the growth rate. In order to keep this advantage and still preserve the process selectivity, the films are prepared at rather high substrate temperatures in the absence of H_2 (He, Ar as carrier gases).[171, 190, 226] If high selectivity of the process is required, another variant is used in which such a substrate or barrier layer material is selected where water molecules are adsorbed poorly.[205]

Analysis of the dependence of the properties of the growing copper film, which is formed upon decomposition of (HFA)Cu(VTMS) vapour, on the thickness of the primary copper layers on SiO_2 showed [397] that the highest deposition rate of copper is observed at a copper layer thickness of 4 nm, and the lowest SER of the film is observed at a thickness of 15 nm. The selectivity of the CVD process with the use of this CCC in the Cu/SiO_2 system at temperatures below 200 °C depends on the carrier gas and on the CCC vapour partial pressure.[304]

Awaya *et al.*[229] conducted a comparative study of the effect of the β-diketone excess on the rate and selectivity of CVD of copper strips upon decomposition of $Cu(HFA)_2$ and (HFA)Cu(VTMS) vapour. The copper strips were deposited in the presence of water vapour on copper substrates with SiO_2 templates previously sputter-deposited on the surface, at a substrate temperature of 390 °C. It was found that the optimum (fast and selective) process for the preparation of copper strips involves two stages. In the first stage, the substrate is treated with H(HFA) vapour in the presence of H_2; after that, $Cu(HFA)_2$ is fed into the reactor and reduced on the substrate in the presence of H_2. However, the presence of a free β-diketone in the stage of $Cu(HFA)_2$ reduction results in the loss of selectivity.

In the case where (HFA)Cu(VTMS) vapour is used in CVD processes, copper with a sputter-deposited SiO_2 template was also used as the substrate; the substrate temperature was 160 – 180 °C. It was shown that, unlike in the experiment with the $Cu(HFA)_2$ vapour described above, the presence of H(HFA) in the stage of strip formation increases the rate of filling the template channel; however, this completely suppresses the process selectivity, as distinct strip edges could not be obtained. It is believed [229] that such a different behaviour of copper(I) and copper(II) compounds in this case is due to the difference between their decomposition mechanisms. Optimisation of the CVD process for film deposition with the use of vapour of copper(I) derivatives and similar templates was considered by Norman *et al.*[398]

Some increase in selectivity can be achieved by the preparation of copper strips on the same substrates, *viz.*, Cu/SiO_2 (template), from (HFA)Cu(VTMS) vapour. This is due to the fact that adsorption of the precursor molecules on SiO_2, which decreases selectivity, depends directly on the presence of reactive hydroxy groups on the substrate surface.[386, 399] Therefore, to exclude a decrease in selectivity, it was suggested [399] to pre-treat the SiO_2 surface with dichlorodimethylsilane vapour. This compound eliminates the reactive OH groups from the SiO_2 surface, thus creating unfavourable conditions for adsorption and film growth at these sites. Nevertheless, as the overall process selectivity is controlled by several factors (*e.g.*, the substrate temperature and the dichlorodimethylsilane vapour pressure), it is difficult to obtain reproducible results.

The selective deposition of copper films can also be provided by using thermally grown SiO_2 as the substrate.[400, 401] In this case, the presence of H_2 during the process [which is usually the case for processes based on Cu(II) derivatives] is an unfavourable factor for the selectivity, as it results in reduction of the SiO_2 surface layer and generation of OH groups.[402]

A study of nucleation upon decomposition of (HFA)Cu(VTMS) on a SiO_2 surface 'freed' from the OH groups showed that under these conditions, an increase in the flow rate of the starting CCC virtually does not affect selectivity;[403] the pressure in the reactor becomes the main parameter for controlling selectivity.

Cu(HFA)(1,5-COD) manifests certain selectivity with respect to the substrate material: the formation and growth of copper films on the surfaces of such dielectrics as SiO_2 and Si_3N_4 occurs with much greater difficulty than on metal substrates.[334] However, this effect is not observed at sufficiently high temperatures (> 200 °C).[330]

A very high selectivity in the deposition of copper films in 'metal–SiO_2' systems is achieved if Cu(HFA)(PMe_3) and Cu(HFA)(PEt_3) complexes are used.[331]

An unexpectedly high selectivity with respect to SiO_2 was shown by copper(I) pyrazolyl borate complexes as the starting CCC upon deposition on Pt/SiO_2, Au/SiO_2, Al/SiO_2 and W/SiO_2 substrates.[372] However, this effect was not observed on the Pd/SiO_2 substrate relative to SiO_2.

2. Use of substrates made of polymeric materials in CVD processes

The use of polymers as substrate materials in CVD processes has certain advantages. For example, it was found that the chemisorption of precursor molecules and the adhesion of copper films to polyimide substrates are much weaker than in the case of SiO_2; this fact enables highly selective deposition.[404] CVD processes with the use of Teflon for the preparation of copper films have become especially popular.

Teflon is used as a dielectric layer with unique properties, such as high resistivity and small dielectric constant. When combined with the low SER of copper films, this affords a very promising basis for the creation of fast microelectronic devices with short signal delay times.[405]

In this case, selectivity is based on two processes. Laser irradiation of the Teflon surface results in cleavage of the polymer chains with simultaneous formation of cross-links between the chains and perfluorocarbons with short chains in the near-surface layer. Both of these processes result in a strong decrease in the copper adhesion on the irradiated substrate areas.[406] Alkaline etching of Teflon results in partial defluorination of the surface layer to a depth of $\geqslant 300$ nm and, hence, formation of a rough surface enriched with carbon atoms, which favours the efficient adhesion of copper films.[405, 407] Hence, a combination of irradiated and etched zones on a Teflon surface can serve as a template owing to purely mechanical properties.

The principles of 'Teflon technologies' were formulated in a series of papers.[408–410] The process usually includes three stages: alkaline etching, creation of a pattern by KrF laser radiation, and high-selectivity CVD of the film (the copper film remains only on the etched areas). In the best experiments, the deposition rate of up to 1 μm min^{-1} was reached and the SER of the films was ~ 1.8 μΩ cm.[410]

VII. Conclusion

Until 1995 accumulation of basic experimental data and the accompanying development of concepts on the mechanisms of CVD of thin copper films with the use of volatile CCC had occurred. Subsequently, the research in this field reached a qualitatively different level.

Over the last two or three years, a certain decrease in the number of original papers was accompanied by an increase in the number of patents obtained both in the fields of the new volatile CCC, the ways for the synthesis of the already known compounds, and the specific details of CVD processes. This is also true for copper(I) and copper(II) derivatives as the starting CCC: the former are attractive due to the low temperatures of evaporation (sublimation) and decomposition on a substrate and the high film deposition rates; the latter, due to the stability during storage and the rather simple synthesis.

For example, copper(II) 6-ethyl-2,2-dimethyloctane-3,5-dionate was patented as a new starting volatile CCC.[411] A series of patents were obtained for many compounds as potential starting CCC for CVD processes in the series of complexes of Cu(HFA) with silylalkenes[412–415] and silylalkynes.[416] Analysis of the composition and properties of the compounds patented shows that by varying the electronic effects of the substituents at the silicon atom and in the diketonate fragment, it is possible to reach an optimum ratio between the stability of the compound and its ability to decompose at low temperatures.

Let us note some technological patents with the use of (HFA)Cu(VTMS). A two-stage CVD process based on this CCC with addition of H(HFA) vapour[417] and H_2O vapour[418] has been patented. It should probably be expected that the number of patents in this field will increase.

Yet another trend worthy of note is the fast progress in the technologies for the selective deposition of films. The 'Teflon technologies' are a significant but not the only achievement in this field. The first specialised review devoted to these technologies[419] generalised the results obtained by that time. So far, a number of important studies have been completed (see, *e.g.*, Refs 420 and 421) that allow one to state that new microelectronic devices have been created using these technologies.

In our opinion, one more promising field for the application of CVD technologies based on volatile copper(II) and copper(I) compounds is the preparation of copper films doped with other metals within one technological process. For example, is was found that the doping of copper films with zirconium atoms provides a good protection against electromigration with an insignificant increase in SER.[422] The addition of a small amount of $Pd(HFA)_2$ to (HFA)Cu(VTMS) vapour results in a copper film containing $\sim 0.5\%$ Pd, which is completely stable against oxidation in air up to 300 °C (see Refs 423 and 424). Attempts at synthesis of similar films doped with Co (see Refs 425 and 426) and Sn (see Ref. 427) were reported. Further development of studies in this field may well result in new materials with unique properties.

A conceptually similar approach is the development of CVD methods for the integrated deposition (using the same equipment) of a buffer layer onto a silicon substrate and a copper film atop this layer. The first study using this approach made it possible to obtain a copper film with very good characteristics (SER = 1.8 μΩ cm) from (HFA)Cu(VTMS) vapour on silicon substrates with a TiN layer sputter-deposited prior to copper deposition.[389]

Perhaps, the above study reflects the most fundamental trend in the field, *i.e.*, the transition from separate experimental studies on the CVD preparation of copper films with the use of concrete starting volatile copper compounds to the creation of integrated CVD technologies with full optimisation of all the conditions of the process up to the preparation of the final product.

Spectacular examples of this approach include: the complete optimisation of a CVD process based on the industrially produced CCC of the CupraSelect grade ('Schumacher', Germany),[428] the study where the technological approach to super-resolution resists was suggested,[392] and the study suggesting the full-scale CVD production of copper films with SER < 2.0 μΩ cm, deposition rate > 200 nm min^{-1}, good adhesion and selectivity, and with ensured reproducibility of the properties of the batch films.[390] It is obvious that the number of studies in this field will increase.

In addition, the CVD-based preparation of copper films can be a technological component of the production of more complex systems. Recently, a technique for optimal CVD of copper films as an intermediate stage in the production of absorbing layers for solar batteries based on $CuInSe_2$ was developed.[429]

Considerable help in the development of CVD technology for the deposition of copper films is provided by the database for quantum-chemical calculations that has appeared recently. For example, the deposition of copper films from (HFA)Cu(VTMS) vapour in a stream of argon was simulated numerically on a computer using the PHOENICS-CVD program and this database.[430] The calculations made it possible to optimise both the conditions of the process and the equipment.

In conclusion of the topic of the development and creation of volatile copper(I) and copper(II) derivatives, it is necessary to mention the attempts to go from searches for new specific technologically promising substances to the development of a general methodology for the synthesis of starting volatile CCC, based both on the analysis of the crystal and molecular structures of the already existing CCC and on quantum-chemical calcula-

tions of the thermodynamic parameters of crystal – vapour phase transitions. Developments of suitable algorithms are under way,[431,432] and it may well be that this approach has great prospects.

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