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The chemistry of volatile β-diketonates and their application in the synthesis of high-temperature superconducting thin films

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Abstract. We shall examine the fundamental aspects of the chemistry of volatile β-diketonates: the dependence of their volatility on the coordination unsaturation of the complexes, on the structure of the ligands, and on the nature of the metals. The gas-phase thermal stability of the β-diketonates and the structural changes which take place when these compounds are transferred to the gas phase are discussed. The most important results on the synthesis of Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O, and Tl–Ba–Ca–Cu–O by chemical vapour deposition from the gas phase are reported. The bibliography contains 106 references.

I. Methods of preparing epitaxial high-temperature superconducting films

According to recent reports[1] high-temperature superconductors (HTSC) are finding practical applications in thin film form, mainly for the following reason. The best samples of high-temperature superconducting films now being produced have surprisingly high critical current densities. The use of HTSC in thin film form can solve several problems in cryoelectronics. In particular, in devices based on the Josephson effect the required current density (10^2–10^3 A cm^{-2}) can be obtained even with polycrystalline films. Many studies (in particular those based on tunnel spectroscopy, optical methods, etc.) aimed at establishing the physical characteristics of the material and the mechanism of the superconductivity in HTSC have had to be carried out with thin film samples.

The anisotropy of the physical characteristics of the materials is being studied with monocrystalline (epitaxial) HTSC films, of which the best samples have properties closer to those of an ideal crystal than is found in most of the monocrystals now being prepared.[2] Studies of the stability (ageing) of HTSC are also most conveniently carried out with films because chemical or physical instability effects are easily detected in film samples (for example, in studies of the effect of irradiation with high-energy particles on the properties of HTSC). Films are also widely used in the search for new superconductors: in particular, the high-temperature metastable phases NbGe and Nb_3Si have been prepared as thin films.

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Various chemical (as well as physical) methods have been used to prepare HTSC films. According to Schieber[3] the most promising of these is the CVD method (chemical vapour deposition from the vapour phase). The basis of the method is to transport the components of the film to the substrate in the form of the vapours of volatile compounds: the vapours are decomposed on the substrate to give a film of the required composition. Halides, hydrides, or organometallic compounds are used as the volatile compounds; this variant of the method is called MOCVD. The CVD method offers a number of advantages over the PVD (physical vapour deposition) method.

1. The possibility of depositing films of uniform composition and thickness on component parts having a complex configuration. This feature is specially important for HTSC films because it makes possible the production of large current-carrying structures in film form, of magnetic screens, and of other 'nonplanar' components.

2. The possibility of achieving high rates of deposition (up to several micrometres per hour) while maintaining a high-quality product (i. e. while controlling its epitaxial character, density, and crystallinity). In contrast to the physical evaporation methods, in which the need for a high growth rate is met by providing a high-energy flux of particles of the substance to be evaporated, with the consequent danger of decomposing the substrate surface (or the already deposited film), in the CVD method a high production rate is achieved by using a high pressure of the transporting vapour or a high flow rate of the carrier gas.

3. A high reproducibility of the properties of the coatings prepared with constant process parameters.

4. Easy control of the process and flexibility in the choice of the technological regime (especially in changes of the chemical composition of the deposit).

5. The possibility of changing from high-vacuum apparatus to assemblies giving a vacuum of 10 Pa or to flow assemblies operating at pressures of 10^2–10^5 Pa.

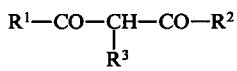
The development of the CVD technology has been fastest in Japan and in the USA. The best samples of HTSC film[4,5] prepared by CVD have been reported from those countries. It should be noted that this type of work is now being carried out, in preference to sustained studies of evaporation in a vacuum by physical methods, in the laboratories of the largest firms active in this field, such as Riken, Nissan Motors, Ori Electronics, Westinghouse, and others. This confirms the favourable prospects of the adoption of the CVD technology in the industrial production of HTSC films.

II. Volatile metal β-diketonates used in CVD technology

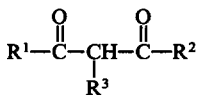
The first and most fundamental problem in the development of the CVD technology is the choice of volatile compounds which satisfy at least the following two requirements: they should have a technologically acceptable vapour pressure and they should pass into the vapour phase (by evaporation or by sublimation) without decomposition, since decomposition of the compound could affect its volatility and thus perturb the constancy of the rate of deposition and of the composition of the film.

In a study of the synthesis of $YBa_2Cu_3O_{7-x}$ the components were transferred through the gas phase as β-diketonates [organometallic chelated complexes having a high volatility at relatively low temperatures (100–300 °C)].

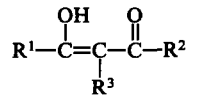
β-Diketones of the general formula



are liquid or solid colourless compounds which exist in two tautomeric forms:

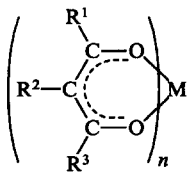


keto form



enol form

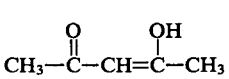
In aqueous solutions β-diketones have weakly acidic properties and react with many metals to give compounds of the chelate type:



where n is the charge on the metal ion. The double bond in the metal ring is delocalised, and the two O–M bonds are equivalent.

Extensive studies of the chemistry of β-diketonates have established quite unambiguously the fundamental principles which determine the relationship between the volatility of these compounds and their composition and structure.[6–8] Since the molecules must overcome the intermolecular interaction forces during evaporation or sublimation, the highest volatility is found in the coordinationally saturated complexes, which do not tend to form oligomers or hydrogen bonds.

Let us examine for example the metal acetylacetonates. When in the enol form



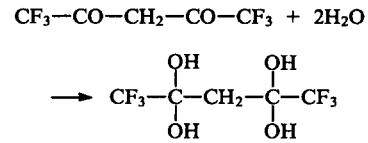
these compounds interact with many metals to give stable uncharged inner complexes (chelates) in which the bond between the metal and the ligands is often covalent. The complexes of acetylacetone with beryllium(II), aluminium(III), and chromium(III) are coordinationally saturated and have a high volatility. On the other hand the acetylacetonates of lithium, sodium, and magnesium are almost completely involatile, probably because of the ionic character of their bond, and also as a result of polymerisation in the condensed phase.

The complexes of the rare-earth elements (REE) with acetylacetone are coordinationally unsaturated, since their c. n. is 8–11, but the β-diketones occupy only six coordination sites in the inner coordination sphere of the metal. Therefore many REE β-diketonates are hydrated and usually contain two or three water molecules. The hydrated metal chelates undergo hydrolytic dissociation when heated, with formation of involatile hydroxy compounds. Furthermore the coordinationally unsaturated β-diketonates of many metals are often oligomerised or polymerised. These compounds have a low volatility and are thermally dissociated when heated.[9]

The replacement of the end methyl groups in acetylacetone by heavier unbranched hydrocarbon radicals (ethyl, n-propyl, n-butyl, phenyl, etc.) produces a change in the volatility of the corresponding complexes. This can be attributed to the increase in the molecular mass, and also to the strengthening of the intermolecular interaction. The latter factor plays a substantial role, because the volatility of the β-diketonates is strongly dependent on the degree of branching of the hydrocarbon end groups. These chelates are less readily hydrated or polymerised. In recent years a strong research effort has been aimed at the β-diketonato complexes of metals with the end methyl groups replaced by *tert*-butyl groups (dipivaloylmethane, DPM).[10–17]

Another indicator of the dependence of the volatility of chelates on the form of the molecule is the fact that the volatility of the REE β-diketonates increases rather than decreases in the series from lanthanum to lutetium, in spite of the increase in molecular mass. Sicre et al.[18] have attributed this effect to the decrease in the ionic radius of the metal (the lanthanide contraction). The result is either a decrease in the intramolecular local dipoles or a better screening from the neighbouring molecules, which weakens the intermolecular interaction forces.

Replacing the hydrogen in the end methyl groups of acetylacetone (AA) by fluorine greatly increases the volatility of the corresponding β-diketonates, evidently (again) as a result of the decrease in the intermolecular interaction forces and of the increased covalency of the metal–ligand bond.[19,20] The coordinationally saturated chelates of hexafluoroacetylacetone (HFA) $CF_3-CO-CH_2-CO-CF_3$ are the most volatile of all the known metal β-diketonates. However, hexafluoroacetylacetone has a serious disadvantage: it reacts with water to give a tetrahydroxy compound:[19]



Therefore the most 'popular' ligand is trifluoroacetylacetone (TFA) $CF_3-CO-CH_2-CO-CH_3$. The volatility of most of its chelates is slightly lower than that of the HFA chelates, but much higher than that of the corresponding acetylacetonates. However, it reacts with water at a negligible rate, and this allows the chelates to be synthesised by extraction of aqueous solutions of the metals with solutions of TFA in organic solvents. The trifluoroacetylacetonates do not tend to form adducts as readily as the hexafluoroacetylacetonates.[8]

Thus the replacement of hydrogen by fluorine increases the volatility of the β-diketonates, but it lowers the thermal stability of the complexes. Therefore some workers[8,21,22] concluded that the most effective complexes are those with β-diketones containing not only a fluorinated radical (which increases the volatility) but also a *tert*-butyl radical (which contributes additional thermal stability). These include pivaloyltrifluoroacetone (PTFA) and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-octan-3,5-dione (FOD), which contain the CF_3 and C_3F_7 radicals respectively. The rare-earth metals form monohydrates with FOD, which are readily dehydrated without decomposition when dried in a vacuum over P_2O_5. The chelates of REE with PTFA can react with uncharged donors with formation of thermally stable complexes.[23]

The volatility of the β-diketonates depends on the nature of the complex-forming metal. For example, films of HTSC can be produced by using complexes of copper with various ligands,

including the complex with acetylacetone, $Cu(AA)_2$, since they all have an adequate vapour pressure and thermal stability (see Table 1).[24–26]

Table 1. Volatile chelated compounds used in the preparation of HTSC films from the vapour phase.

Metal	Ligand		Designation of chelates
	R	R′	
Cu	CH_3	CH_3	$Cu(AA)_2$
Cu, Y, Ba, Sr, Ca	$(CH_3)_3C$	$(CH_3)_3C$	$M(DPM)_n$
Cu, Ba	CF_3	CF_3	$M(HFA)_2$
Ba, Y	C_3F_7	$(CH_3)_3C$	$M(FOD)_n$
Cu	$CH_3-C(=NH)-CH_2-CO-CH_3$		$Cu(Acim)_2$ [a]

[a] Acim is acetylacetoneimine.

The ions of the alkaline earth metals (the components of the HTSC, Sr^{2+} and especially Ba^{2+}) form involatile oligomeric complexes with β-diketones. The freshly prepared complexes of these metals are monomeric and contain between two (the magnesium, calcium, and barium β-diketonates) and four water molecules (the strontium β-diketonates). However, after dehydrating and heating the complexes additional lines are observed in the IR and Raman spectra[27] in the metal–ligand vibration region (400, 650 cm^{-1}) and in the bending region of the chelate ring (600–900 cm^{-1}). Under these conditions the chelates are characterised by a total involatility, and the mass spectra of the complexes indicate the formation of species with a molecular mass well in excess of the molecular mass of the monomeric compound. The appearance of new bands in the IR and Raman spectra after dehydration and heat treatment of the complexes may be associated with polymerisation during dehydration, which is the mechanism most likely to oppose the transfer of compounds to the gas phase. The degree of oligomerisation is strongly dependent on the nature of the central atom and increases with the atomic number of the metal. It has been established that the volatility of the alkaline-earth metal chelates is markedly affected by the method of dehydrating the prepared compounds, and also by the method of storage.[28] The sublimation characteristics of even the most suitable of these complexes for CVD technology (barium dipivaloylmethanate, $BaL_2 \cdot 2H_2O$) are markedly degraded during storage. The results of photoelectron spectroscopy in the gas phase and of thermal analysis have shown that barium dipivaloylmethanate is hydrolysed as follows during storage:

$$BaL_2 \cdot 2H_2O \longrightarrow Ba(OH)L + HL + H_2O .$$

The additional hydration of $BaL_2 \cdot 2H_2O$ during storage favours more extensive hydrolysis. It should be noted that storage over P_2O_5 is also undesirable because this drying agent appears to enhance the hydrolysis by shifting the equilibrium as a result of its interaction with the vapour of the acid (HL) evolved by the hydrolysis of $BaL_2 \cdot 2H_2O$. Large changes in the sublimation properties during the storage of the preparations over P_2O_5 are observed also in the β-diketonates of other metals (for example the REE).[29]

Thus the hydrolysis of $BaL_2 \cdot 2H_2O$ during the storage and subsequent sublimation processes is one of the main causes of instability of this compound. However, an equally important cause may be the slow oligomerisation of the anhydrous barium dipivaloylmethanate. It has been reported[28] that reproducible results on the sublimation of barium dipivaloylmethanate can be obtained by eliminating all the factors which favour polymerisation. One way of solving this problem is to add the BaL_2 in the form of compounds with additional uncharged ligands, $BaL_2 \cdot nQ$ whose inclusion in the composition of the complex suppresses the hydrolysis and favours the depolymerisation of $(BaL_2)_n$ by saturating the coordination sphere of the Ba^{2+} ion with the donor molecules of the additional ligand Q. The complex of the pivaloyltrifluoroacetonate of barium(II) with dimethylformamide has been discussed as an example.[27]

It would seem that the vapour pressure of the barium chelates could be increased by increasing the temperature. However, this method is limited by considerations of the thermal stability of the β-diketonates. The competition between the sublimation and the thermal decomposition of the barium complexes is one of the main problems in the CVD technology for the production of $Y(Ln)Ba_2Cu_3O_{7-x}$. As has already been pointed out[1] this problem can be solved by a careful choice of the sublimation regime and of the method of synthesis of the chelates, aimed at minimising the possibilities of oligomerisation.

III. Structural changes of metal β-diketonates during their transfer to the gas phase

The metal cation is usually attached to the β-diketonate anion through two oxygen atoms belonging to the hydroxyl and the carbonyl group, forming the chelate. However, recent physicochemical studies have shown that other methods of coordinating the β-diketone ligands are possible: in particular, the monodentate coordination of the metal by an oxygen atom. Compounds of this type include the complexes Cu(HFA)(MeNHCH$_3$NHMe), $Cu(AA)_2En_2 \cdot 2H_2O$, $(CH_3)Si(AA)$, and $(CH_3)_3Hg(AA)$, where Me is methylene and En is ethylenediamine.[30–34]

A similar method of coordination is possible also at temperatures close to the thermal dissociation temperature. ESR studies and studies by electronic and IR spectroscopy have shown that during the transfer to the gas phase at high temperatures the c. n. of the complex decreases as a result of the opening of the chelate ring. This effect is most clearly seen in compounds containing an additional electron donor molecule, for example $M(HFA)_2 \cdot 2TBPO$, where M = Co, Ni, Cu and TBPO is tributylphosphine oxide.[35,36] From the standpoint of thermodynamics this means that at least in the gaseous state the metal β-diketonates can exist as an equilibrium of two isomeric forms: a chelate and an open ring. The quantitative relationship between the bidentate and the monodentate form depends both on the temperature and on the energy of the M–O bond in the complex. Because of their structure the metal β-diketonates with a monodentate coordination should be chemically more active towards addition and exchange reactions.

It has been shown[37] that the vapour formation process is accompanied by exchange reactions induced by three

$$ML_n \rightleftharpoons ML_{n-1} + L^{\cdot} , \quad (1)$$

$$M'L'_n \rightleftharpoons ML'_{n-1} + L'^{\cdot} , \quad (2)$$

$$ML_n + L'^{\cdot} \rightleftharpoons ML_{n-1}L' + L^{\cdot} , \quad (3)$$

$$M'L'_n + L^{\cdot} \rightleftharpoons M'L'_{n-1}L + L'^{\cdot} \text{ etc.} \quad (4)$$

mechanisms. The first is the radical–chain mechanism:

The second mechanism is the formation of polymeric species in the condensed or the gaseous phase followed by dissociation

$$kML_n(\text{sol., gas}) + lM'L'_n(\text{sol., gas}) \rightleftharpoons (MM'L_nL'_n)_{k+l}(\text{sol., gas}), \quad (5)$$

$$(MM'L_nL'_n)_{k+l}(\text{sol., gas}) \begin{cases} \longrightarrow lML_{n-1}L'(\text{gas}) + kM'L'_{n-1}L(\text{gas}) \\ \longrightarrow lML'_n(\text{gas}) + kM'L_n(\text{gas}) . \end{cases} \quad (6)$$

into monomeric molecules during vapourization:
This mechanism probably applies to the exchange reactions between the β-diketonates which can either have an oligomeric structure in the condensed state or form dimeric molecules in the gas phase.

The third ligand exchange mechanism is possible when the β-diketonates exist in an open form. Under these conditions unstable polymeric molecules exist on the surface of the condensed phase, where they can subsequently dissociate into the initial complex and a mixed complex:

$$ML_n \rightleftharpoons ML_{n-1}L^* , \quad (7)$$

$$M'L'_n \rightleftharpoons M'L'_{n-1}L'^* , \quad (8)$$

$$ML_{n-1}L^* + M'L'_{n-1}L'^* \rightleftharpoons \{MM'L_nL'_n\} \rightleftharpoons ML_{n-1}L'^* + M'L'_{n-1}L , \quad (9)$$

where L* (L'*) is a ligand with monodentate coordination.

The possible occurrence of all the above mechanisms must be borne in mind when superconducting films are synthesised from the gas phase by the pyrolysis of organometallic compounds. Thus, it has been shown[38] by IR spectroscopy that when a mixture of gaseous $Cu(AA)_2$ and $Ba(DPM)_2$ is heated in an argon atmosphere at 200 °C a redistribution of the ligands is observed, leading to the formation of the involatile complexes $Ba(AA)_2$ and Ba(AA)L which perturb the stoichiometric relationship between Ba and Cu. In order to avoid uncontrolled changes in stoichiometry during the deposition of BaO and CuO/Cu_2O on an oriented Si(100) face the use of copper dipivaloylmethanate has been recommended as the source of the Cu phase.

IV. Gas-phase thermal stability of yttrium, barium, copper, calcium, and bismuth β-diketonates, used in CVD technology

The β-diketonates of elements such as yttrium, barium, copper, bismuth, etc. are used as the initial components for the synthesis of HTSC thin films by chemical deposition from the vapour phase. Data on the thermal stability of these compounds and on the effect of oxygen on the thermolysis process have been reported,[39–46] and the mutual effects of the β-diketonates during thermolysis have been discussed.

According to mass spectrometric results the main gaseous products of the thermal decomposition of the yttrium, copper, and barium acetylacetonates are acetone and ethylene. Passing from copper to barium increases the ethylene content of the thermolysis products from 22 to 87 mol%. By combining kinetic data with an analysis of the product we may conclude[39] that the thermolysis of $M(AA)_n$ takes place by an intramolecular process in the coordination sphere of the metal. The first step of this process is the opening of the chelate ring, followed by the breaking of the M–O and C=C bonds in the case of $Cu(AA)_2$ and of the C=C bond in the case of yttrium and barium chelates.

Changing to fluorine-substituted β-diketones gives thermolysis products with a more complex composition.[40] Thus the products of the thermal dissociation of the calcium, strontium, barium, and yttrium, trifluoroacetylacetonates are trifluoroacetone, trifluoromethanol, trifluoroethane, trifluoromethane, acetone, ethanol, carbon dioxide and monoxide, ethylene, hydrogen fluoride, and methane. The relative amounts of these products are determined by the nature of the metal. In the case of trifluoroacetylacetone (TFA) the main thermal decomposition product was trifluoroacetone, whereas for the derivatives of strontium, barium, and yttrium the main products were carbon dioxide and monoxide. Replacing the actylacetonato ligand by its fluorine-substituted analogue lowers the thermal stability of the calcium derivatives five-fold. The β-diketonates can be arranged in the following series of decreasing thermal stability:[41]

$$(AA)_2Ca > (TFA)_2Ca \approx (PTFA)_2Ca > (TFA)_2Sr.$$

In a study[42,43] of the sublimation of yttrium and barium dipivaloylmethanates it was established that $Y(DPM)_3$ sublimes in two steps at 130 and 160 °C. Evidently this effect is due to the formation of dimers. The ratio of dimers to monomers is 1 : 3. Barium dipivaloylmethanate sublimes at 300 °C. A mass spectrometric study has shown that the sublimed product is a trimer in the gas phase, and according to a thermal study of the vapour of the chelate complex the thermolysis is preceded by a depolymerisation process. A combination of mass spectrometric and DTA methods has been used[44] to study the thermal decomposition of the vapours and of the solid phase for bismuth chelates of general formula $Bi(R-CO-CH_2-CO-R')_3$, where $R = CF_3$, $R' = CH_3$, CF_3, $C(CH_3)_3$, $C(CH_3)_2OCH_3$. From an analysis of the mass spectra it was concluded that the vapour of these compounds consists of BiL_3 monomers. The volatility of the complexes with respect to the form of the substituent R' decreases in the sequence $C(CH_3)_2OCH_3 > C(CH_3)_3 > CH_3 > CF_3$. In the thermolysis of the chelate vapours the gaseous products are β-diketones and their fragments.

In a study of the thermal decomposition of the solid phase of the bismuth β-diketonates it was noted that in a flow of helium and oxygen the β-diketonates containing trifluoroacetylacetone and hexafluoroacetylacetone as ligands decompose at 100–150 °C. The thermal stability of the complexes containing *tert*-butyl groups rises to 300 °C, and these complexes are less likely to form oligomers because of the steric factors associated with the bulky substituents of the ligands in the octahedral bismuth complex. The increase in the steric factor produced by the replacement of the $C(CH_3)_3$ substituent by $C(CH_3)_2OCH_3$ suppresses the dimerisation of the molecules almost totally and thus allows the sample to be sublimed repeatedly with a yield of 90%–95%.

The thermal stability of the β-diketonates in the gas phase is strongly influenced by the presence of oxygen, which is added to the reaction volume, and of other volatile β-diketones (the initial complexes for the synthesis of the HTSC).[45,46] Thus the thermal stability threshold of the vapour of copper dipivaloylmethanate *in vacuo* is 330 ± 10 °C, whereas in the presence of oxygen it falls to 280 ± 10 °C. For the vapour of yttrium dipivaloylmethanate the stability threshold is 490 ± 10 °C. Oxygen lowers this threshold to 395 ± 5 °C. It was shown that the vapour of copper dipivaloylmethanate affects the thermolysis of yttrium dipivaloylmethanate in oxygen. Since the vapour of the $Cu(DPM)_2$ complex has a lower thermal stability than the vapour of $Y(DPM)_3$ a shortage of oxygen is produced in the reaction region during the thermolysis of the vapour of the yttrium complex. This raises the decomposition threshold to the temperature level observed in the absence of added oxygen.

A study of the thermal stability of the yttrium, barium, and copper β-diketonates with various ligands allowed Bykov et al.[46] to choose the optimum conditions for the deposition of layers at pressures of 1–5 torr on substrates of monocrystalline silicon and of sodium silicate glass in a reactor of the bell-jar type with heated walls, three heated evaporators, and an oxygen admission tube. The organometallic compound was introduced in a stream of argon.

The maximum growth rate of the copper, barium, and yttrium oxides obtained from the corresponding dipivaloylmethanates was found to occur at 530–550, 600–620, and 550–560 °C respectively. The rate of growth of the films of copper oxide from the acetylacetonate decreased at temperatures above 550 °C, probably as a result of the partial decomposition of the organometallic compound in the reactor volume. The optimum temperatures of the evaporators of the β-diketonates for the synthesis of films at suitable rates have been determined. For $Cu(AA)_2$, $Cu(DPM)_2$, $Y(DPM)_3$, $Ba(DPM)_2$ they are 110–140, 90–120, 60–120, and 210–260 °C respectively.

V. Use of CVD technology in the synthesis of high-temperature superconducting films

1. Y–Ba–Cu–O films

The volatility of β-diketonates under equilibrium conditions is determined by the temperature dependence of the saturated vapour pressure. The vapour pressures of the β-diketonates used in the synthesis of $YBa_2Cu_3O_{7-x}$ have been reported.[6,18,47,48] However, under real conditions these results are not always reproducible because non-equilibrium conditions tend to be established in flow-through reactors, which must be used because of the low volatility of the chelate compounds of barium and also because of the need to reconcile the sublimation and vapour transport conditions with the conditions for the oxidative thermal decomposition of the volatile compounds near the substrate surface.

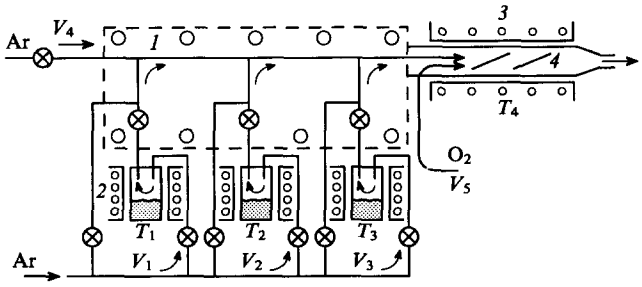


Figure 1. Apparatus for depositing coatings from the gas phase. T_1-T_3 are the temperatures of the evaporators (bubbler type); T_4, temperature of the substrate; V_1-V_3, flow rates of the inert gas (Ar) passing through the evaporators; V_4, flow rate of the inert gas (Ar) passing through the gas collector; V_5 flow rate of the oxygen; the arrows denote the directions of the gas flows; *1* gas collector, *2* evaporators, *3* heaters, *4* substrate.

A typical CVD apparatus[49,50] for the preparation of $YBa_2Cu_3O_{7-x}$ thin films is shown in Fig. 1. In these assemblies the independently variable parameters are the temperatures of the substrate and of three evaporators of the bubbler type, the rates of five gas flows (the flows of inert gas through the three bubblers and through the gas collector, and the flow of oxygen over the substrate), and the total pressure in the reactor. We know that the homogeneity region for the cations in the $YBa_2Cu_3O_{7-x}$ phase is very narrow, and therefore even small departures from stoichiometry induce the formation of a second phase. To avoid this danger a very precise control must be applied to the flow rates of the inert gas (~1%) and to the evaporator temperatures (~0.1 K).

Difficulties are also met in the construction of the 'hot' flow controllers at the outlet of the evaporators and of the hot collector, whose temperatures must not fall below the temperature of the evaporators (in order to avoid condensing the sublimed vapours). The vapours of the β-diketonates and of their thermal decomposition products can interact with the material of the reactor walls. Therefore the reactor must be constructed with an inert material or with materials coated with silver, which does not form stable β-diketonates. Quartz cannot be used because at high temperatures the hot quartz walls could absorb barium from the vapour (forming the stable barium silicate).

Let us examine the results of some studies of the synthesis of $YBa_2Cu_3O_{7-x}$ by the CVD technology,[51–56] using as the initial components the dipivaloylmethanates of yttrium, barium, and copper. The total flow of carrier gas in the three evaporators was 0.3 $dm^3\ min^{-1}$; the pressure in the horizontal quartz reactor was 660–1300 Pa. Depositing the condensate at a rate of 0.8–1.0 μm h^{-1} on a polycrystalline substrate of $ZrO_2(Y_2O_3)$ heated to 800 °C produced film with zero resistance at 45 K with inclusions of textureless[51,52] $BaCuO_2$ and CuO. Raising the temperature of the substrate to 900 °C improved the quality of the films: at a thickness of 0.8–1.0 μm they consisted of preferentially oriented crystallites (with the *c* axis perpendicular to the plane of the substrate, the so-called type 001 texture), and they began to enter the superconducting state at $T_c^H = 89$ K, $T_c(\rho = 0) = 80$ K. The best transition into the superconducting state was obtained by slowly cooling the films in a stream of oxygen ($p_{O_2} = 10^5$ Pa).[53,54] Textured films 2 μm thick with zero resistance at 84 K and a critical current density of 2×10^4 A cm^{-2} (at 77 K and the zero magnetic field *H*)[55] were obtained at 900 °C on a monocrystalline $SrTiO_3$ substrate cut in the (100) plane.

By lowering the substrate temperature to 850 °C (thus suppressing the chemical interaction at the film–substrate interface) Yamane [56] obtained the film with the best transport properties, having the following parameters at 77 K:

H/T	27	8	1	0
J/ A cm^{-2}	6×10^4	2.2×10^5	4.8×10^5	10^6.

In this case the total flow rate of the carrier gas (argon) was 0.45 $dm^3\ min^{-1}$, the flow rate of oxygen was 0.25 $dm^3\ min^{-1}$, and the pressure in the reactor was 130 Pa. The sublimation of $Cu(DPM)_2$, $Y(DPM)_3$, and $Ba(DPM)_2$ was carried out at 136, 145, and 253 °C respectively. The rate of growth of the film was 1–6 μm h^{-1}. By using masking techniques Muto[57] and Watanabe [58] obtained superconducting films 1 μm thick having $T_c = 92$ K and a high value of J_c ($10^5 - 10^6$ A cm^{-2} at 77 K in a magnetic field of up to 30 T).

Superconducting films have been obtained[5,59] on monocrystalline MgO by separating in time the condensation of the oxides and the solid-phase formation reaction of the superconducting phase. The dark brown condensate obtained at 400–600 °C was roasted in oxygen at 800–920 °C and was then slowly cooled. The $YBa_2Cu_3O_{7-x}$ films were converted into the superconducting state over a wide range of temperatures: 80–20 K (Berry[5]) and 76–60 K (Nakamori[59]).

Zhang et al.[60] have claimed slightly better characteristics for their superconducting films. The temperature of the onset of superconductivity was $T_c^H = 93$ K, and zero electrical resistance of the Y–Ba–Cu–O film was observed at 84 K. Good results have been obtained by using the two-stage technology.[61–63] Thus, Noh et al.[61] synthesised semitransparent films which had a resistance of >10 MΩ at a thickness of 1 μm on substrates of $SrTiO_3$ [oriented (100)] in a rotating high-speed disk reactor. After heat treatment at 860–980 °C the $YBa_2Cu_3O_{7-x}$ films became superconducting, some of the samples having $T_c = 90$ K and a transition width $\Delta T_c < 2$ K. Schmaderer et al.[62] used yttrium, barium, and copper 2,2,6,6-tetramethylheptan-3,5-dionates (TMHD), having evaporation temperatures of 112, 208, and 117 °C respectively, to prepare $YBa_2Cu_3O_{7-x}$ thin films on polycrystalline substrates of stabilised ZrO_2 and on monocrystalline $SrTiO_3$ (100) substrates, which were roasted at temperature ≥850°C. On these films the authors found $T_c > 90$ K, $\Delta T_c = 0.2–0.5$ K. The maximum critical current density J_c on a ZrO_2 substrate was 6×10^3 A cm^{-2} at 77 K, whereas on an $SrTiO_3$ substrate the films had $J_c \approx 10^6$ A cm^{-2} in a zero magnetic field and 10^5 A cm^{-2} in a field of 5.5 T. By using the same β-diketonates films of Y–Ba–Cu–O have been obtained[63] on substrates of stabilised $ZrO_2 + Y_2O_3$ and $BaF_2 + ZrO_2/Y_2O_3$. After being heat treated at high temperatures the best films on the $BaF_2 - ZrO_2/Y_2O_3$ substrate had $T_c^H \approx 100$ K and $T_c(\rho = 0) = 80$ K.

The low volatility of the barium β-diketonates (including its dipivaloylmethanate) has been repeatedly pointed out.[5,21,50,59] Therefore even at high flow rates through the bubbler (0.5 $dm^3\ min^{-1}$ for a bubbler temperature of 253 °C) the growth rate of the films is unacceptably slow.[5] Raising the temperature of the bubbler to 300 °C does not usefully improve the growth rate

because it lowers the effectiveness of the barium source.[21,50] To increase the volatility some workers[21,22,49] have used fluorinated β-diketonates, but high rates of deposition of the films were not invariably achieved. Thus, when using barium hexafluoroacetylacetonate[49] with an evaporator temperature of 220 °C the rate of deposition was only 0.3 μm h^{-1}. The use of barium 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctan-4,6-dionate increased the rate of deposition of the film to 1.6 μm h^{-1} in a stream of argon (0.3 dm^3 min^{-1}) for an evaporator temperature of 170 °C. For a rate of supply of argon of 1 dm^3 min^{-1} and an evaporator temperature of 350 °C the growth rate of the film rose[22] to 4.6 μm h^{-1}.

The use of fluorinated β-diketones introduces serious complications into the phase transition process during the synthesis of $YBa_2Cu_3O_{7-x}$ by the CVD method. Even in an oxygen atmosphere the decomposition of the fluoro-organic complexes of barium at 400–1000 °C leads to the formation of the thermally stable BaF_2. This is confirmed by a study[64] in which copper acetylacetonate and yttrium dipivaloylmethanate were mixed with barium hexafluoroacetylacetonate. After heat treatment in an oxygen atmosphere at 900 °C a mixture of Cu_2O, CuO, Y_2O_3, $Cu_2Y_2O_5$, and BaF_2 was formed.

To convert BaF_2 into an oxide phase some workers have used a mixture of oxygen and water vapour.[21,22,65] As has been pointed out,[65,66] in order to shift the equilibrium of the reaction

$$BaF_2 + H_2O \longrightarrow BaO + 2HF \qquad (10)$$

towards the right we need a large excess of water vapour in comparison with the HF. Thus, at 830 °C $\Delta G < 0$ if $p_{H_2O}/p_{HF} > 10^5$, and at 1200 °C $\Delta G < 0$ if $p_{H_2O}/p_{HF} > 10^3$.

In practice the process takes place under nonequilibrium conditions: the inert gas or the oxygen, saturated with water vapour, removes the HF from the reaction volume, which corresponds to conversion, and the resulting BaO reacts with the CuO and Y_2O_3. In a gas stream saturated with H_2O at 23 °C reaction (10) begins[22] at 550 °C. But BaF_2 can be incorporated in the film in substantial amounts even at high temperatures. The inclusion of the BaF_2 conversion stage into the kinetics of the solid-phase formation reaction of $YBa_2Cu_3O_{7-x}$ and the presence of water vapour (which assists the mass transfer in oxide systems) alter the morphology of the films as compared with those prepared from compounds not containing fluorine. The predominance of crystallites with their *a* axis oriented perpendicular to the substrate in these films has been pointed out.[22] However, it is also accepted[1] that the effect of residual fluorine on the properties of the film is still not understood.

Reaction (10) proceeds more smoothly if the evolved HF is trapped as SiF_4 by interacting with SiO_2. This requires the use of quartz reactor walls or alternatively the addition of a special charge of SiO_2. It has been shown[66] that films prepared in the presence of SiO_2 have a zero resistance at 89 K whereas in the absence of SiO_2 the superconducting state is reached only at 50 K. The best films of $YBa_2Cu_3O_{7-x}$, prepared by using fluorinated yttrium, barium, and copper β-diketonates, are characterised[22,67,68] by a temperature of transition to the superconducting state in the region of 70–90 K.

Some of the published work deals with the effect of various factors on the processes of deposition from the vapour phase and with the preparation of superconducting Y–Ba–Cu–O films of high quality (i.e. with high values of T_c and J_c). Thus, several workers[69–71] have determined the effect of the substrate material on the parameters of the superconducting film. The β-diketonates were deposited on different substrates, including MgO(100), $SrTiO_3$(100), ZrO_2(100), sapphire(1102), pure metals, and metals covered with a buffer layer of polycrystalline $SrTiO_3$. The best results (T_c = 90 K and ΔT_c = 2 K) were obtained[71] on $SrTiO_3$(100) substrates. These workers introduced the metal chelates into the reaction chamber in a stream of N_2 at temperatures above 100 °C. The residual pressure in the chamber was 1.01 × 10^4 Pa, and the oxygen partial pressure was 5.06 × 10^3 Pa. Singh et al.[72] tried to increase the stability of the film towards atmospheric degradation by depositing on the substrate a preliminary buffer layer of BaF_2. By chemically depositing $Y(TMHD)_3$, $Ba(TMHD)_2$, and $Cu(TMHD)_2$ from sources at temperatures of 150–250 °C on to a silicon substrate heated to 700 °C they obtained superconducting films with parameters T_c^H = 90 K and $T_c(\rho = 0)$ = 73 K.

Sugii et al.[73] studied the effect of the heat treatment temperature of the substrate on the properties of films prepared by the deposition of yttrium, barium, and copper 2,2,6,6-tetramethylheptan-3,5-dione complexes at temperatures in the range of 600–700 °C on monocrystalline $SrTiO_3$(100). It was established that the crystallinity, which was degraded by lowering the substrate temperature (T_c = 71 and 10 K for substrate heating temperatures of 650 and 600 °C respectively), could be restored by lowering the rate of addition of oxygen during the deposition process.

Attempts to lower the working temperature of the substrate by using a modified plasma method of chemical deposition from the vapour phase have been reported.[74–77] The presence of a plasma substantially alters the mechanism of film formation: the atomic mechanism is replaced by an atomic–ionic (or purely ionic) mechanism, which offers a large energy gain during compound formation. The Y–Ba–Cu–O films prepared at 580 °C had T_c = 82 K and $J_c = 10^6$ A cm^{-2} (at 50 K).[77] The effect of the vapour pressure of the organometallic compounds on the quality of the films has been studied.[78,79] It was found[78] that lowering the vapour pressure increases the $T_c(\rho = 0)$ temperature of the superconducting transition from 66 to 83 K. At the same time by lowering the pressure from 1.33 × 10^3 to 6.67 × 10^2 Pa the volatility of the yttrium and copper chelates was increased while that of the barium chelate remained unchanged, causing a depeltion of barium in the film. In order to obtain films of stoichiometric composition Kim et al.[79] increased the amount of the charge of barium 2,2,6,6-tetramethylheptan-3,5-dione in the reactor: this allowed them to prepare films of stoichiometric composition on an MgO substrate with T_c = 91 K (ΔT_c = 2 K), whereas on a substrate of $SrTiO_3$ they produced films with a critical current density of 10^5 A cm^{-2} in a zero magnetic field at 77 K.

The effect of the oxygen source (O_2, H_2O, O_2 + H_2O or N_2O) on the chemical deposition from the vapour phase of Y–Ba–Cu–O films by using metal β-diketonates containing (or not containing) fluorine atoms has been discussed.[80] The best conditions for the deposition of chelates without fluorine are found at low pressures and by using N_2O as the source of oxygen. With chelates containing fluorine better results are obtained by using O_2 and H_2O, but in this case the region of deposition of the required phase is narrowed. In a study[81] of the dependence of J_c and T_c on the thickness of $YBa_2Cu_3O_{7-x}$ films (0.2–2.4 μm), produced by coevaporation and heat treatment in O_2 and water vapour at 850 °C for 3.5 h on $SrTiO_3$(100) substrates it was found that J_c decreases exponentially from 1 × 10^6 to 4 × 10^3 A cm^{-2} as the film thickness is increased, whereas T_c falls from 90 to 85 K.

Khoroshun et al. [82] have proposed a new and apparently simpler aerosol method of chemical deposition of organometallic compounds from the gas phase. The main feature of this method is that predetermined amounts of the initial materials are introduced as aerosols into the reaction volume. Very thin monocrystalline $YBa_2Cu_3O_{7-x}$ films were prepared in this way. Films of thickness $d \geqslant 80$ nm had $T_c(\rho = 0)$ = 78–80 K and $\Delta T_c \approx 2$ K. The critical current density was 10^7 A cm^{-2} at 4.2 K in a magnetic field of 5 T. Thinner films (d = 10 nm) had $T_c(\rho = 0)$ = 50 K, $\Delta T_c \approx 13$ K.

2. Bi–Sr–Ca–Cu–O films

The preparation of Bi–Sr–Ca–Cu–O films is complicated by the existence of many cuprates of bismuth and of the alkaline

earths in this system, with similar thermodynamic characteristics.[83] The problem of the volatility of the initial components, which created the main difficulties in the synthesis of the Y–Ba–Cu–O films, is now of secondary importance because the β-diketonates of strontium and calcium are much more volatile than the corresponding barium compounds.[8] Bismuth is usually introduced as one of the volatile alcoholates or as a BiR_3 compound with various alkyl or aromatic radicals, because the β-diketonates of bismuth have not been adequately studied. A description of the synthesis and properties of the bismuth β-diketonates has been published very recently.[84]

Films of Bi–Sr–Ca–Cu–O have been synthesised[85,86] by using bismuth ethoxide and calcium, strontium, and copper dipivaloylmethanates. The deposits were produced on $ZrO_2(Y_2O_3)$ and MgO substrates at 800 and 900 °C respectively. Using a deposition rate of 8 μm h^{-1} gave superconducting films with T_c = 70–80 K and a tetragonal (or pseudotetragonal) lattice.

Several workers[87–93] used triphenylbismuth $Bi(C_6H_5)_3$ as the initial component for the deposition of Bi–Sr–Ca–Cu–O films. Some of these,[87,88] by combining this reactant with the β-diketonates of calcium, strontium, and copper, working at 550 °C, and heat treating the deposit in a stream of oxygen at 600–865 °C, obtained a superconducting film with T_c = 78.8 and ΔT_c = 7.7 K on an MgO(100) substrate (with some CuO phase as an impurity). An X-ray phase analysis of this system[88] detected the presence of a $Bi_2(Ca, Sr)_3Cu_2O_x$ phase with T_c = 85 K, and traces of phases with the lattice parameter c = 24.4 or 37 Å and T_c = 110 K. Bi–Sr–Ca–Cu–O films have been grown[89,90] on substrates of monocrystalline $SrTiO_3$(100) by using as the initial components triphenylbismuth, and also calcium, strontium, and copper 2,2,6,6-tetramethylheptan-3,5-dionates[89] and the fluorocarbon chelates of the same metals.[90] The use of lower pressures and a plasma gave[89] a single-phase film with its crystallographic c axis in a preferential orientation normal to the substrate surface. Nemoto and Yamana[90] used a horizontal quartz reactor with a residual pressure of ~1 Pa, and after heat treatment of the product they obtained films with T_c = 80 K and a zero resistance at 50 K.

Zhang et al.[91] described the synthesis of Bi–Sr–Ca–Cu–O films by the deposition of triphenylbismuth, copper acetylacetonate, and strontium and calcium dipivaloylmethanates on a polycrystalline silver substrate at 625–700 °C. Their films are a mixture of the $Bi_2(Sr, Ca)_2CuO_x$ and $Bi_2(Sr, Ca)_2Cu_3O_x$ phase, the proportion of the phase with T_c = 110 K increasing with the decomposition temperature. A study of these films by scanning electron microscopy showed that the deposition on polycrystalline silver greatly improves the texture and the morphology of the films as compared with those prepared on a magnesium oxide substrate. This effect was attributed to the nucleating properties of silver for films of the 2212 phase. The critical current density of these films was ~3.9×10^5 A cm^{-2} at 5.5 K.

The Bi-containing films were doped with lead in order to stabilise the high-temperature phase.[92] Bi–Pb–Sr–Ca–Cu–O films were prepared by two methods. In the first method the lead was introduced by depositing (alternately) Bi–Sr–Ca–Cu–O and PbO_x layers, using the volatile organometallic compounds $Cu[(CH_3)_2CHCOCOCH_3]_2$, $Sr[CH_2(COC(CH_3)_3)_2]_2$, $Ca[CH_2(COC(CH_3)_3)_2]_2$, $Bi(C_6H_5)_3$, and $Pb(C_6H_5)_4$. In the second method the lead was introduced in the initial deposition of the Bi–Sr–Ca–Cu–O film by using PbO as the source. The addition of lead greatly improves the crystal orientation and morphology of the films. On MgO(100) substrates films consisting mainly of the $Bi_2(Sr, Ca)_3Cu_2O_x$ phase were obtained, with T_c^H and $T_c(\rho = 0)$ equal to 110 and 80 K respectively. The formation of HTSC on MgO substrates at 850 °C has been monitored[93] by electron microscopy and X-ray phase analysis. It was established that the 2212 phase (with the lower critical temperature) is deposited during the early stages of the process. The 2223 phase is formed from the low-temperature phase after 30 min. Films 8 nm thick begin to be converted into the superconducting state at 110 K, and zero resistance is reached at 21 K.

Thus it follows from the results considered above that all the following modifications contribute to the stabilisation of the high-temperature $Bi_2SrCa_2Cu_3O_{10}$ with T_c = 110 °C: heating the substrate, plasma treatment during the growth of the film (followed by heat treatment), partial replacement (up to 30%) of the bismuth by lead, and a lengthy final heat treatment.

Volatile halides ($BiCl_3$, CuI_2, CaI_2, SrI_2), heated together in a single stream of inert gas, have been used[94–97] as the initial components for the synthesis of the films. In one method[94] the halides were placed in the tubular quartz reactor of a horizontal gradient furnace, each compound being located in a different temperature region: 150–250 °C for $BiCl_3$, 450–600 °C for CuI_2, 750–850 °C for CaI_2 and 800–850 °C for SrI_2. At the same time the substrate (heated to 800–850 °C) was placed in the region where the halide vapours came into contact with the water vapour entering the reactor with the external stream of inert gas, giving a pyrohydrolysis reaction. The film thus produced had the composition $BiSr_{0.8}CaCu_{3.7}O_x$, T_c = 70–80 K, and a critical current density of ~10^4 A cm^{-2} at 10 K. Films of a better quality were obtained[95] by omitting the additional heat treatment in oxygen. The films were deposited on an MgO(001) substrate at 700–850 °C from a gaseous mixture of halides which had reacted with oxidising agents (O_2 and H_2O). The films, of average thickness 0.1 μm, consisted of a mixture of phases with low or high critical temperatures (~80 and ~110 K). The films deposited at 850 °C had a zero resistance at 98 K. Their critical current density was ~1.7×10^4 A cm^{-2} at 4.2 K. The authors point out that the characteristics of the films depend both on the concentration of oxygen and on the deposition temperature. The structure of Bi–Sr–Ca–Cu–O, thin films deposited on MgO(001) from their chlorides or iodides with helium as the carrier gas and oxygen as the oxidising agent has been studied[97] by transmission electron microscopy. The best films, having a superconducting transition temperature of ~100 K, were oriented along their c axis, and consisted of large domains with an average size of 15–100 μm. Five types of layer were identified in the structure of the Bi–Sr–Ca–Cu–O films along the c axis, with crystal structures of the perovskite type and different thicknesses. It was pointed out that the phase with T_c = 80 K is predominant in these films, whereas the phase with T_c = 110 K is present in much smaller quantities.

3. Tl–Ca–Ba–Cu–O films

In the synthesis of films of high-temperature superconductors in the Tl–Ca–Ba–Cu–O system we again meet the problem of many possible phases. However, there are also other difficulties. Because of the high toxicity of thallium conventional evaporators cannot be used. To avoid contaminating the surface of the apparatus the toxic thallium compounds have to be kept in traps cooled in liquid nitrogen.[98] Because of the high volatility of the oxide Tl_2O_3 the heat treatment temperature of the thallium films must be very accurately controlled. However, the high volatility of thallium oxide can be exploited in the technological process for saturating the Ba–Ca–Cu–O film with the vapour of this compound.[99–102]

Lin and Wu[99] placed a Ba–Ca–Cu–O film prepared by magnetron evaporation in an Al_2O_3 boat at the centre of a tube furnace which also contained a crucible filled with powdered thallium oxide. After holding the charge for 15–60 min at 925 °C a film with $T_c^H \approx$ 120 K and zero resistance at 78 K was obtained. The main superconducting phase was the 2122 phase, which was found to contain large quantities of $BaCuO_2$, $CaCuO_2$, CuO, and other impurities. Other workers[100] used both pure thallium oxide and a mixture of powdered Tl_2O_3, BaO_2, CaO_2, and CuO heated at 895 °C to impregnate a film of Ba–Ca–Cu–O prepared by the pyrolysis of the salts of organic acids. This method gave thick films with T_c^H = 126 K and zero

resistance at 108 K, the high-temperature 2223 phase being dominant in the second case.

The use of massive ceramic samples as sources of thallium oxide allows films of stoichiometric composition to be synthesised, because the reaction takes place under thermodynamic equilibrium conditions.[83] The best film samples, containing mainly the highly oriented $Tl_2Ca_2Ba_2Cu_3O_{10+y}$ phase and traces of the $Tl_2CaBa_2Cu_2O_{8+y}$ phase were obtained[102] at 895–900 °C (in the region of the Ba–Ca–Cu–O film sample) and 810–805 °C (in the region of the Tl_2O_3 boat). These films had $T_c(\rho = 0) = 95-105$ K and a critical current density of 28 800 A cm^{-2} at 77 K in a zero magnetic field. It is pointed out that the films with the highest critical current densities have a highly textured structure consisting of platelet crystallites.

The preparation of high-temperature superconductor films in the Tl–Ba–Ca–Cu–O system by the direct CVD method has been reported.[103–106] Ba–Ca–Cu–O films were synthesised[103] on $ZrO_2(Y_2O_3)$ substrates using barium heptafluorodimethyloctandionate, calcium dipivaloyldimethanate, and copper acetylacetonate as the initial components. The thallium was introduced by two methods: as the gas phase from a solid source containing Tl, Ba, Ca, and Cu, and as the organometallic compound cyclopentadienylthallium. The films thus obtained consisted mainly of the $TlBa_2Ca_2Cu_3O_x$ phase with T_c = 100 K. Highly oriented epitaxial films of the 2122 phase with T_c > 105 K were synthesised[104] by decomposing organic compounds of thallium, calcium, barium, and copper on the surface of an MgO(100) crystal. By doubly annealing $Tl_2CaBa_2Cu_2O_y$ on sapphire substrates at 850 and 500 °C (the first anneal being in the presence of $Tl_2CaBa_2Cu_2O_y$ wafers for 40 min) Zhang et al.[105] increased $T_c(\rho = 0)$ from 87.5 to 94 K, but the films were contaminated by traces of the $BaCO_3$ and Ca_2Cu_3O phase. The best samples of thallium films were synthesised by Hamaguchi et al.,[106] who prepared oriented films of $Tl_2Ba_2Ca_{1.4}Cu_2O_x$ and $Tl_2Ba_2Ca_{2.3}Cu_3O_x$ by chemical deposition in the gas phase on monocrystalline MgO(100) substrates. The stoichiometry of the films was preserved by annealing them in dry oxygen in the presence of Tl_2O_3 vapour at 850–900 °C. These films had T_c^H and $T_c(\rho = 0)$ equal to 125 and 109 K respectively, and their critical current density was 10^4 A cm^{-2} at 90 K

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This analysis of published results in the chemistry of volatile β-diketonates has shown that because of their high volatility at relatively low temperatures and of their thermal stability these materials have been widely applied in the synthesis of thin films of high-temperature superconductors containing yttrium, bismuth, and thallium.

The volatility of the β-diketonates is determined by their composition and structure, and depends on the nature of the complex-forming metal, on the coordinational saturation of the complexes, and on the degree of branching of the hydrocarbon end groups. The highest volatility is found in the coordinationally saturated complexes, which do not readily form oligomers or hydrogen bonds. Replacing the hydrogen in the end methyl groups by fluorine causes a large increase in the volatility. In order to improve the thermal stability we can use complexes containing a *tert*-butyl radical as well a a fluorinated radical.

In the gaseous state the metal β-diketonates exist as two isomeric forms in equilibrium: the chelate and the open ring. The quantitative relationship between the bidentate and the monodentate coordinated forms depends both on the temperature and on the energy of the M–O bond in the complex. The possible mechanisms of the exchange reactions in the vapour formation process discussed above should be allowed for when thin films are synthesised from the gas phase. The thermal stability of the β-diketonates in the gas phase is strongly influenced by oxygen, and also by the presence of other volatile β-diketonates, used as the initial components for the synthesis of the thin films. The high quality and the characteristics of the high-temperature superconducting films prepared in many laboratories by CVD confirm that this method offers very attractive prospects.

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