

Reviews

THERMODYNAMIC MODELLING OF CVD OF HIGH- T_c SUPERCONDUCTORS

A. Hårsta

Thin Film and Surface Chemistry Group, Department of Inorganic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Abstract

Thermodynamic modelling of CVD of the superconducting phases in the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems is reviewed. Both MOCVD and halide CVD are considered. The results are discussed in terms of calculated CVD stability diagrams. The influence of deposition parameters, including selection of precursors, on the existence and extension on those stability regions, where the superconducting phases can be deposited, is described. The results of the thermodynamic modelling are compared with experimental investigations. The agreement between thermodynamics and experiments is satisfactory, indicating that thermodynamic modelling can be used as a guide to predict the optimum deposition conditions.

Keywords: CVD, high- T_c superconductors, thermodynamic modelling

Introduction

Since the discovery of superconductivity in the La-M-Cu-O systems, where $M = \text{Ca, Sr or Ba}$ [1], research efforts have been intense in the field of these new oxide superconductors. New representatives with much higher critical temperatures, T_c , have been detected in e.g., the Y-Ba-Cu-O [2], Tl-Ba-Ca-Cu-O [3], Bi-Sr-Ca-Cu-O [4] and Hg-Ba-Ca-Cu-O [5] systems. One of the most challenging tasks is to be able to prepare high-quality thin films of these materials. This would be beneficial both for basic research and practical applications. Thin films of the oxide superconductors have been prepared by many deposition techniques, among others chemical vapour deposition (CVD). The CVD technique has many advantages: the microstructure and texture can be controlled; the method has an excellent step coverage; extremely dense films can be prepared; the defect content of the film can be carefully controlled; and easy to scale up and uniform coatings are obtained over large areas. The CVD method has also successfully been used to deposit superconducting films in the Y-Ba-Cu-O, the Bi-Sr-Ca-Cu-O and the

Tl-Ba-Ca-Cu-O systems (for a review see e.g. [6]). The latter compound is invariably prepared by a two-step process where a Ba-Ca-Cu-O film is first prepared followed by incorporation of thallium by a vapour diffusion process (see e.g. [7]). However, this paper will only consider CVD in the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems.

In CVD of high- T_c superconducting materials, two main types of precursors can be distinguished. In the first and most common method, usually referred to as MOCVD (metal organic chemical vapour deposition), different metal chelates are used. The notation MOCVD is, however, not strictly correct since the metal chelates do not contain any metal-carbon bonds but only metal-oxygen bonds. MOCVD have been employed in the vast majority of all CVD experiments (see e.g. [6]). The alternative method is to use metal halides as precursor material. This has been successfully demonstrated in both the Y-Ba-Cu-O [8] and the Bi-Sr-Ca-Cu-O [9] systems.

Several different compounds have been employed as metal precursors in MOCVD of the superconducting phases in the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems. With the exception of bismuth, metal chelates have invariably been used. They have the general formula $R_1\text{-CO-CH-CO-R}_2$, where R_1 and R_2 denote either an alkyl group or a fluorosubstituted alkyl group. For the element bismuth, the most common compound is $(\text{C}_6\text{H}_5)_3\text{Bi}$, triphenyl bismuth. Furthermore, different oxygen sources such as O_2 , H_2O , $\text{O}_2 + \text{H}_2\text{O}$ and N_2O have been used.

A survey of the literature (see e.g. [6]) reveals that a deposition temperature of at least 700°C is generally needed to obtain the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase in situ. However, some exceptions should be noted. First, it has been observed that by using plasma-activated CVD, the superconducting compound can be obtained at a lower temperature. An excimer laser activated process has also been reported to reduce this temperature. Moreover, by using N_2O as the oxygen source, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase can be obtained at a somewhat lower deposition temperature (about 650°C , see e.g. [10]). A recent paper has even reported MOCVD of superconducting films at as low temperature as 500°C using N_2O [11]. Also a low total pressure and a low oxygen partial pressure have been reported to reduce the required deposition temperature.

One of the problems in MOCVD of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is codeposition of BaCO_3 and BaF_2 . Formation of carbonate at low deposition temperatures (650°C) has been observed by several authors (see e.g. [12, 13]). Also formation of BaF_2 has been observed when employing fluorine-containing precursors at low deposition temperatures (see e.g. [14, 15]). In one of these studies [14], the amount of BaF_2 was found to be reduced when H_2O was used as oxygen source instead of O_2 . This was explained by the reaction between H_2O and fluoride yielding oxide and HF. Finally, in addition to BaF_2 , also YF_3 has been detected [15].

For in situ deposition of superconducting Bi-Sr-Ca-Cu-O films by MOCVD, a deposition temperature of at least 750°C is required [6]. It should be noted that the Bi-Sr-Ca-Cu-O system contains several superconducting phases, e.g., the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ phase (Bi-2212) with $T_c \sim 85$ K and the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ phase (Bi-2223) with $T_c \sim 110$ K [16]. However, the majority phase obtained by CVD is invariably the Bi-2212 phase. This agrees well with the larger thermodynamic stability of this phase compared to the Bi-2223 phase [17]. Lead has been reported to promote the formation of the Bi-2223 phase and Pb-doped Bi-Sr-Ca-Cu-O films have been

prepared [18]. However, the Bi-2212 phase constituted the majority phase also here, but an increased c-axis orientation was reported. It can also be noted that a higher deposition temperature has been found to increase the amount of the Bi-2223 phase [19].

As mentioned above, a problem in MOCVD of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase is codeposition of carbonates and fluorides. In MOCVD of the Bi-2212 phase, fluorine has been reported to be incorporated in the films [20, 21]. This contamination was, however, removed in the annealing process. It has also been reported that all four metal components cannot be deposited using water as the only oxygen source, but that the presence of oxygen is necessary to deposit bismuth [22].

Only a few investigations exist where halides have been employed as metal precursors in CVD of superconductors. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase has been deposited using a mixture of chlorides and iodides (YCl_3 , BaI_2 and CuI) as metal precursors [8]. A mixture of H_2O and O_2 was used as the oxygen source and the total pressure was 2.67 kPa. The superconducting phase was obtained without post-annealing between 870 and 910°C. A mixture of chlorides and iodides (BiCl_3 , SrI_2 , CaI_2 and CuI) has also been employed for deposition of the Bi-2212 and Bi-2223 phases [9]. Again a mixture of H_2O and O_2 was used as the oxygen source and the total pressure was 100 kPa. Superconducting films were here obtained between 700 and 850°C. This temperature could be reduced to 580°C by using plasma-enhanced CVD [23]. The Bi-2212 phase has recently also been deposited using exclusively iodides as metal precursors and with O_2 as the only oxygen source [24]. The total pressure was 1.33 kPa and superconducting films were obtained between 780 and 810°C.

When designing an experiment for CVD of the superconducting phases, i.e., compounds consisting of four or five elements, many parameters can be varied. First suitable source materials for the components have to be selected. Other variables include the deposition temperature, the total pressure and the inlet partial pressures of the gaseous precursors. For such a multiparameter system, thermodynamics can be used as a guide to predict the deposition conditions. This has been demonstrated for CVD of the superconducting phases in both the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems (both halide CVD and MOCVD) by our group [25-30]. For the Y-Ba-Cu-O system, such modelling has also been performed by Vahlas and Besmann [31, 32] and Pisch *et al.* [33, 34] (MOCVD) and by Ilyinyh *et al.* [35] (halide CVD). A study of a more limited scope of CVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase from chloride precursors has also been reported [36]. The present paper constitutes a review of results obtained from thermodynamic modelling of CVD of high- T_c superconductors in the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems. The results obtained by our group will be the starting point, but comparisons will be made with other investigations. The thermodynamic predictions will finally also be compared with experiments.

Thermodynamic modelling

The CVD stability diagrams

All diagrams presented in this review have been obtained using the computer program EKVICALC [37]. The program is based on the free-energy minimisation

technique [38, 39]. The input parameters are the temperature, the total pressure, the amounts of the starting materials and thermodynamic data for all substances in the data base that consist of the starting elements. The output are the equilibrium composition of the system, i.e., the amounts of condensed phases and the partial pressure of gaseous species and various thermodynamic quantities, e.g., ΔG (change in Gibbs free-energy). The results of the calculations are presented in calculated CVD stability diagrams. The diagrams in this review are considerably simplified compared to those in Refs [25–30], where both the phase composition and the yield of the superconducting phases were given. Here only those regions where the superconducting phases can be deposited have been indicated by means of a grey shade.

As mentioned before, a problem in MOCVD of the superconducting phases in both the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems may be codeposition of carbonates and fluorides. Such contaminations can precipitate to the grain boundaries and may thus affect the current density to a large extent. The regions in the CVD stability diagrams where the superconductor is accompanied by carbonates or fluorides are therefore not considered useful to deposit the superconducting phase.

The CVD stability diagrams were obtained from thermodynamic calculations using different metal precursors and oxygen sources as starting materials (see below). The calculations were repeated for different total pressures, temperatures and oxygen source to metal source ratios. In the diagrams, the position of the region where the superconducting phase can be deposited is given as a function of the deposition temperature for a specific oxygen source to metal source ratio. For the Y-Ba-Cu-O system, this latter quantity is defined as:

$$([\text{O}_2] + [\text{H}_2\text{O}] + [\text{N}_2\text{O}]) / ([\text{YX}_a] + [\text{BaY}_b] + [\text{CuZ}_c])$$

where the brackets denote the amount in mole of a specific compound and X, Y and Z denote the ligands. For the Bi-Sr-Ca-Cu-O system, it is defined as:

$$([\text{O}_2] + [\text{H}_2\text{O}] + [\text{N}_2\text{O}]) / ([\text{BiX}_a] + [\text{SrY}_b] + [\text{CaZ}_c] + [\text{CuV}_d]),$$

where X, Y, Z and V denote the ligands.

Thermodynamic data

The Y-Ba-Cu-O system

For deposition of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, the input ratio between the three metal components was fixed to 1:2:3 in the CVD stability diagrams. This ratio is supported by the stoichiometry of the phase and also by the nearly quantitative yield of the individual binary oxides upon deposition. The substances included in the calculations and the sources of thermodynamic data can be found in Refs [25, 28, 29]. It should be noted that several thermodynamic data sets have been given for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, e.g. [40, 41]. The data given in Ref. [40] for the composition $\text{YBa}_2\text{Cu}_3\text{O}_7$ were used in the first paper [25]. These calculations did not include any ternary or quaternary oxides, since no thermodynamic data were reported for these

phases. In the later papers [28, 29] the data given by Lee *et al.* [41] were used, since they also provided data for ternary and quaternary oxides. The data for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase were now given for the composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$. The selected composition for the superconducting phase affects the position as well as the size of the region where this phase can be deposited. The CVD stability diagrams of the first paper [25] should therefore not be compared to any exactness to the corresponding diagrams of later papers [28, 29].

It should be emphasised that the non-stoichiometry of the superconducting phase was not taken into consideration [25, 28, 29]. However, this has been made in the calculations presented by Vahlas and Besmann [32] and Weiss *et al.* [34]. A comparison with their results will be made in later sections.

For MOCVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, thermodynamic calculations were made for several combinations of metal chelate precursors [29]. The oxygen sources chosen were O_2 , H_2O , $\text{O}_2+\text{H}_2\text{O}$ and N_2O . It should be observed that no thermodynamic data exist for the metal chelates. In the calculations, these compounds were substituted by a combination of the pure metals and hydrocarbons or fluorine-containing hydrocarbons to obtain the correct stoichiometry [29]. This will not affect the CVD stability diagrams, since they only reflect the final state of the system at equilibria. The driving force values are affected, but these quantities are not considered in the present work.

For halide CVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, thermodynamic calculations have been made for both a mixture of chlorides and iodides [25] as well as for only chlorides and only iodides [28]. The oxygen sources employed were O_2 , H_2O or a mixture of $\text{O}_2+\text{H}_2\text{O}$.

The Bi-Sr-Ca-Cu-O system

In the CVD stability diagrams for deposition of the Bi-2212 phase in the Bi-Sr-Ca-Cu-O system, the input ratio was chosen to be 2:2:1:2. As for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, this ratio is supported by the stoichiometry of the phase and by the nearly quantitative yield of the binary oxides upon deposition. The substances included in the calculations and the sources of thermodynamic data can be found in Refs [26, 27, 30]. It should be emphasised, that no ternary or quaternary oxides were included in the calculations in this system. Furthermore, no thermodynamic data have been reported for the superconducting phases in the Bi-Sr-Ca-Cu-O system. However, the largest gain in free-energy occurs when the binary oxides are formed. Rather small decreases in free-energy are expected when going from the binary oxides to the ternary, quaternary and superconducting oxides, respectively. The regions in the CVD stability diagrams where only the four binary oxides (Bi_2O_3 , SrO , CaO and $\text{CuO}/\text{Cu}_2\text{O}$) are deposited, were thus considered to be the regions in which the superconducting Bi-2212 phase can be deposited (denoted the Bi-2212 region in the following). This is also supported by the results from thermodynamic calculations in the Y-Ba-Cu-O system [25]. As mentioned above, thermodynamic data have been reported for the superconductor in this system. It was found that the position and size of the regions in the CVD stability diagrams where the

superconductor can be deposited followed the same trends upon changing the deposition conditions as the regions where only the binary oxides can be deposited. In the latter calculations the superconducting phase was omitted from the calculations. However, the size of these regions were found to be considerably smaller.

For MOCVD of the Bi-2212 phase, thermodynamic calculations were made for several combinations of metal precursors [30]. The oxygen sources chosen were O_2 , H_2O , O_2+H_2O and N_2O . As for MOCVD of the $YBa_2Cu_3O_{7-x}$ phase, no thermodynamic data exist for the metal precursors. Again these compounds were substituted by a combination of the pure metal and hydrocarbons or fluorine-containing hydrocarbons to obtain the correct stoichiometry [30].

For halide CVD of the Bi-2212 phase, thermodynamic calculations have been made for both a mixture of chlorides and iodides [26] as well as for only chlorides and only iodides [27]. The oxygen sources employed were O_2 , H_2O or a mixture of O_2+H_2O .

Results of the modelling

The Y-Ba-Cu-O system

MOCVD

The results of the thermodynamic calculations are summarised in Fig. 1. It should be emphasised that these diagrams should only be used as a guide to how the deposition conditions are affected when the deposition parameters are varied. The arrows in the diagrams indicate if the region where the $YBa_2Cu_3O_{7-x}$ phase can be deposited is reduced or enlarged when such a parameter is changed. The length of an arrow indicates the relative importance of the change. In these tentative CVD stability diagrams, the border-line of the $YBa_2Cu_3O_{7-x}$ region has been drawn with O_2 as the reference oxygen source.

For fluorine-free precursors, the largest $YBa_2Cu_3O_{7-x}$ region is obtained when O_2 is replaced by N_2O as the oxygen source [29]. This may be due to the fact that

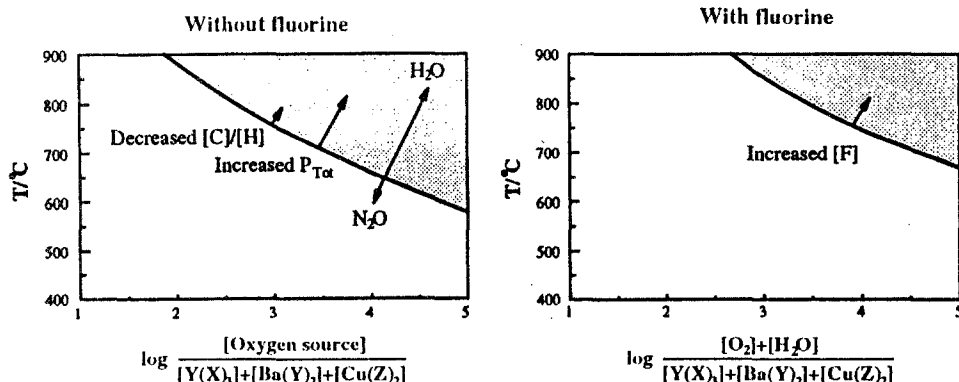


Fig. 1 CVD stability diagram showing qualitatively the influence of critical deposition parameters on the stability region of $YBa_2Cu_3O_{7-x}$ for precursors without and with fluorine

small amounts of NO(g) is formed, which will lower the total energy of the system and thus lower the temperature where an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region is obtained. Using H_2O as the oxygen source, no $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region can be obtained [29]. This is due to the presence of large amounts of hydrogen resulting from the decomposition of H_2O , which yields a reducing atmosphere preventing the formation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. Furthermore, a decreased total pressure and a precursor with a higher carbon/hydrogen ratio is advantageous to gain a large $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region [29]. The effect of the latter parameter is, however, very small. When the total pressure is decreased, the partial pressure of CO_2 will simultaneously decrease. BaCO_3 then becomes less stable towards decomposition to BaO , which will shift the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region to a lower temperature. It can also be seen that a rather high deposition temperature has to be used, which is necessary to prevent the formation of BaCO_3 [29]. The deposition temperature can be reduced if a larger oxygen source to metal source ratio is used.

For fluorine-containing precursors, an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region can only be obtained using an $\text{O}_2 + \text{H}_2\text{O}$ mixture as the oxygen source [29]. However, the size of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region is considerably smaller than the corresponding size for precursors without fluorine. The need for both O_2 and H_2O can be explained as follows. Using only H_2O will result in large amounts of hydrogen from the decomposition of H_2O , which will give a reducing atmosphere preventing the formation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. On the other hand, when O_2 is used as the only oxygen source, BaF_2 is present in all parts of the CVD stability diagram. Hydrogen in H_2O is thus required to take care of fluorine and form HF. As for precursors without fluorine, a rather high deposition temperature has to be used. This is necessary to prevent the formation of BaF_2 [29].

It is interesting to compare these results with other thermodynamic modelling studies. Vahlas and Besmann [31, 32] found that a low total pressure was advantageous to obtain a large $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region. They also found it beneficial to use a high partial pressure of oxygen. These results are in excellent agreement with the results obtained in our group. In the study of Pisch *et al.* [33] the $\text{BaCO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ equilibrium was investigated, and it was found that it should be beneficial to use N_2O as the oxygen source. The same group [34] also found a low total pressure and a low carbon content of the precursor to be advantageous to deposit the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. This is also in good agreement with our results, except for the effect of the carbon content. However, as mentioned above, the influence of this parameter was very small in our study.

Halide CVD

For chloride precursors, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase cannot be deposited when O_2 is used as the only oxygen source [28]. If H_2O is used as the only oxygen source, it is possible to deposit this phase, but the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region is rather small. As can be seen in Fig. 2a, this region can be expanded by using a mixture of $\text{O}_2 + \text{H}_2\text{O}$. It can also be seen that a rather high oxygen source to metal source ratio is necessary to deposit the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. This ratio can be reduced if a higher deposition temperature is employed. However, the highest yield is obtained at a low tempera-

ture [28]. Furthermore, the largest $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region is obtained using a high total pressure, which simultaneously shifts the region towards a higher oxygen source to metal source ratio and a higher temperature [28].

For iodide precursors, the best deposition conditions are obtained by using only O_2 as the oxygen source. As can be seen in Fig. 2b, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region occupies almost the entire CVD stability diagram. In contrast, only a rather small $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region is obtained using H_2O as the oxygen source. As for chloride precursors, the highest yield is obtained using low deposition temperatures and a high total pressure [28].

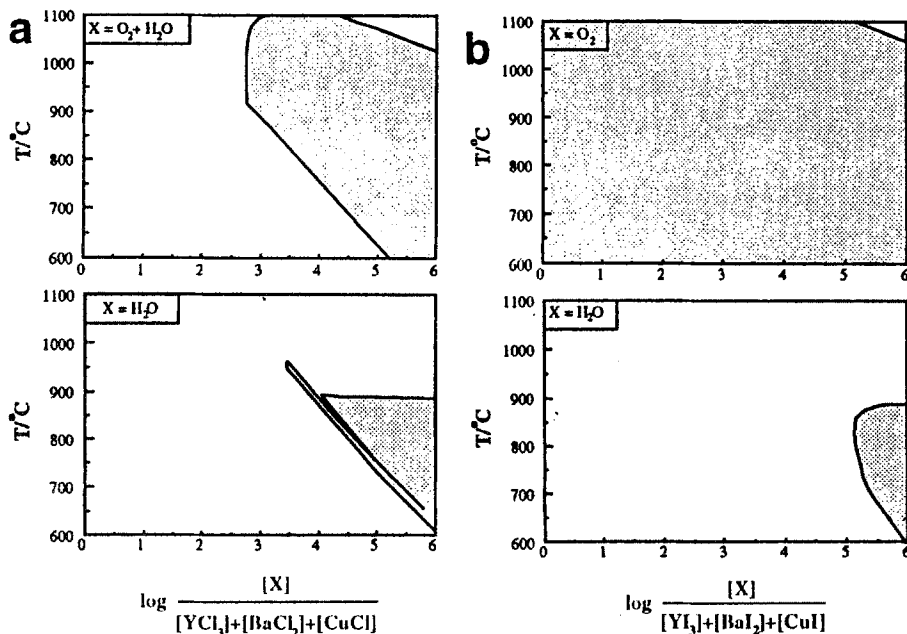


Fig. 2 Schematic CVD stability diagram for the $\text{YCl}_3\text{-BaCl}_2\text{-CuCl-O}_2\text{-H}_2\text{O}$ and $\text{YCl}_3\text{-BaCl}_2\text{-CuCl-H}_2\text{O}$ systems. The ratio $[\text{H}_2\text{O}]/[\text{O}_2]$ is 1/1 in the top diagram (a) ; Schematic CVD stability diagram for the $\text{YI}_3\text{-BaI}_2\text{-CuI-O}_2$ and $\text{YI}_3\text{-BaI}_2\text{-CuI-H}_2\text{O}$ systems (b)

As a conclusion, thermodynamic calculations predict that it should be advantageous to use iodide precursors instead of chloride precursors for halide CVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. Both a large size of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region and a high yield of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase are favoured by using iodides instead of chlorides. Furthermore, O_2 can be used as the only oxygen source, while H_2O is necessary to deposit the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase from chloride precursors. This is explained by the lower stability of the metal iodides compared to the metal chlorides. Moreover, for chloride precursors no $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ region can be obtained when O_2 is the only oxygen source. The presence of H_2O is thus necessary in the chloride case. The chlorine in the metal chlorides is taken care of by H_2O and forms HCl , which is the main chlorine-containing reaction product in this reaction. In contrast, for iodide

precursors the main iodine-containing reaction products are I and I₂. These can be formed without the presence of H₂O. The advantage of using, iodides instead of chlorides was also confirmed by Ilyinyh *et al.* [35]. However, they predicted a different pressure dependence, i.e., that a low total pressure should be used.

The Bi-Sr-Ca-Cu-O system

MOCVD

The results of the calculations have been summarised in Fig. 3. As for the corresponding CVD stability diagram for deposition of the YBa₂Cu₃O_{7-x} phase (Fig. 1), the arrows indicate if the Bi-2212 region is reduced or enlarged when a deposition parameter is changed. The border-line of the Bi-2212 region is drawn with O₂ (F-free precursors) or O₂ + H₂O (F-containing precursors) as the reference oxygen source.

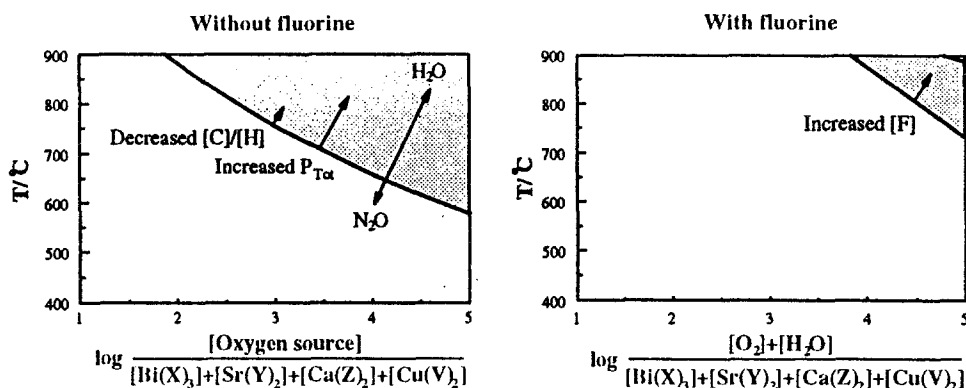


Fig. 3 CVD stability diagram showing qualitatively the influence of critical deposition parameters on the Bi-2212 stability region for precursors without and with fluorine

For precursors without fluorine, the influence of the oxygen source is the same as for MOCVD of the YBa₂Cu₃O_{7-x} phase, i.e., the largest Bi-2212 region is obtained using N₂O as the oxygen source and no such region can be obtained using H₂O as the only oxygen source [30]. This latter effect is due to the presence of large amounts of hydrogen resulting from the decomposition of H₂O, which yields a reducing atmosphere preventing the formation of the binary oxides Bi₂O₃ and CuO/Cu₂O. Also the influence of the total pressure and the carbon/hydrogen ratio is the same as for MOCVD of the YBa₂Cu₃O_{7-x} phase. It can also be seen that a rather high deposition temperature has to be used. This is necessary to prevent the formation of SrCO₃. The deposition temperature can be reduced by employing a larger oxygen source to metal source ratio.

For fluorine-containing precursors, a Bi-2212 region can only be obtained using an O₂ + H₂O mixture as the oxygen source [30]. However, the size of this region is considerably smaller than the corresponding size for precursors without fluorine. The explanation to the need for both O₂ and H₂O is the same as given above for MOCVD of the YBa₂Cu₃O_{7-x} phase. Furthermore, a very high deposition temperature is needed. This is necessary to prevent the formation of SrF₂.

Halide CVD

The results of the calculations have been summarised in Fig. 4. All results regarding trends when the deposition conditions are changed are essentially the same as for halide CVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase. The main difference is that no Bi-2212 region can be obtained using iodide precursors and H_2O as the only oxygen source, while a corresponding region exists in the Y-Ba-Cu-O system. It should also be noted that the size of the Bi-2212 regions is somewhat smaller than the corresponding regions in the Y-Ba-Cu-O system. However, this may be explained by the inclusion of ternary and quaternary oxides in the latter system. As mentioned before, omission of such phases has been found to result in smaller regions in the CVD stability diagrams where the superconductor can be deposited.

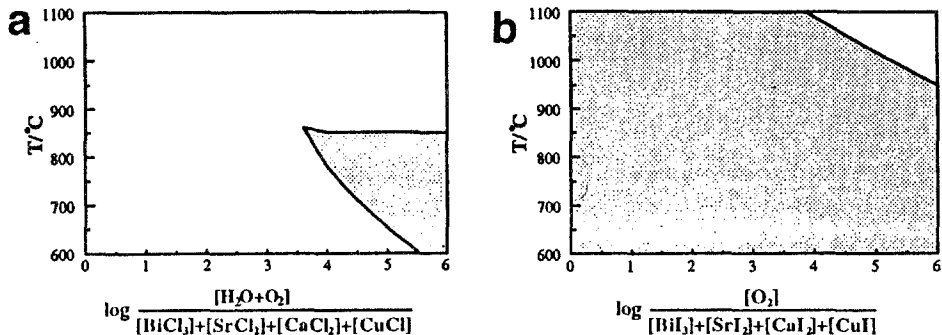


Fig. 4 Schematic CVD stability diagram for the BiCl_3 - SrCl_2 - CaCl_2 - CuCl - O_2 - H_2O system. The ratio $[\text{H}_2\text{O}]/[\text{O}_2]$ is 1/1 in the top diagram (a); Schematic CVD stability diagram for the BiI_3 - SrI_2 - CaI_2 - CuI - O_2 system (b)

Comparison with experiments

The primary aim with thermodynamic modelling is to be able to predict how the deposition conditions are affected when the experimental parameters are changed. It may thus be of interest to compare the results of the thermodynamic modelling reviewed here with experimental results.

For MOCVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase, a low total pressure has been reported to yield higher critical temperatures [40], and should thus be beneficial for depositing the superconducting phase. Furthermore, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase could be deposited at a lower temperature when N_2O was used as the oxygen source than with O_2 [10, 11, 41]. For fluorine-containing precursors, H_2O has been reported to be superior to O_2 as oxygen source for the deposition of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase [14]. The effect of H_2O was suggested to be the removal of fluorine in the form of HF. However, the superconducting phase was only obtained after annealing in O_2 . The presence of both O_2 and H_2O thus seems to be desirable. All these results agree well with the thermodynamic predictions. However, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase has also been reported to form *in situ* at as low a temperature as 650°C when a very low partial pressure of O_2 was employed. When the partial pressure of O_2 was in-

creased, no superconducting phase could be deposited. This is in contrast to the results of the thermodynamic modelling, which predict a high oxygen source to metal source ratio to be advantageous for a low deposition temperature.

For MOCVD of the Bi-2212 phase in the Bi-Sr-Ca-Cu-O system, a rather high temperature ($\sim 750^\circ\text{C}$) has been reported to be required for *in situ* deposition [6]. Furthermore, the presence of O_2 is necessary, i.e., no Bi-2212 phase can be deposited using only H_2O as the oxygen source [22]. This is in good agreement with thermodynamics. The thermodynamic calculations predict that N_2O should be the best oxygen source. Only a few investigations exist in the Bi-Sr-Ca-Cu-O system using N_2O as the oxygen source [42, 43], but the superconducting phase was not obtained *in situ*. However, it is likely that the deposition temperatures used ($625\text{--}700^\circ\text{C}$) were too low. Using fluorine-containing precursors, no Bi-2212 phase has been obtained without post-annealing of the deposited layers [20, 21]. According to the results of the thermodynamic calculations, a mixture of O_2 and H_2O is required for deposition of the superconducting phase and both these studies used only O_2 as the oxygen source.

As mentioned in the introduction, only a few experimental investigations exist using halide precursors in CVD of the superconducting phases in the Y-Ba-Cu-O and the Bi-Sr-Ca-Cu-O systems. For halide CVD of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase a mixture of chlorides and iodides was used as source materials [8]. The presence of both O_2 and H_2O was found to be necessary to deposit the phase and, furthermore, high oxygen source to metal source ratios were required. For halide CVD of the Bi-2212 phase and when using a mixture of chlorides and iodides, a mixture of O_2 and H_2O was invariably employed (see e.g. [9]). All these results are in good agreement with thermodynamics. Furthermore, as predicted by thermodynamics, it was recently shown that it is possible to deposit the Bi-2212 phase with only O_2 as the oxygen source when exclusively iodides were used as metal precursors [24].

As a conclusion it has been shown that the agreement between thermodynamics and experiments are quite satisfactory. This suggests that thermodynamics can serve as a guide to predict the optimum deposition conditions. Thermodynamics may thus be a useful tool when designing CVD experiments of high- T_c superconductors.

* * *

Financial support from the Swedish National Board for Industrial and Technical Development is gratefully acknowledged.

References

- 1 J. G. Bednorz and K. A. Müller, *Z. Physik B* 64 (1986) 189.
- 2 M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.*, 58 (1987) 908.
- 3 Z. Z. Sheng, A. M. Hermann, A. Elali, C. Almasan, J. Estrada and R. J. Matson, *Phys. Rev. Lett.*, 60 (1988) 937.
- 4 H. Maeda, Y. Tanaka, M. Fukutomi and T. Asho, *Jpn. J. Appl. Phys.*, 27 (1988) L209.
- 5 A. Schilling, M. Cantoni, J. D. Guo and H. R. Ott, *Nature*, 363 (1993) 56.
- 6 M. Leskelä, H. Mölsä and L. Niinistö, *Supercond. Sci. Technol.*, 6 (1993) 627.

- 7 G. Malandrino, D. S. Richeson, T. J. Marks, D. C. DeGroot, J. L. Schindler and C. R. Kannewurf, *Appl. Phys. Lett.*, 58 (1991) 182.
- 8 M. Ottosson, T. Andersson, J.-O. Carlsson, A. Hårsta, U. Jansson, P. Norling, K. Niskanen and P. Nordblad, *Appl. Phys. Lett.*, 54 (1989) 2476.
- 9 M. Ihara, T. Kimura, H. Yamawaki and K. Ikeda, *IEEE Trans. Magn.*, 25 (1989) 2470.
- 10 T. Tsuruoka, R. Kawasaki and H. Abe, *Jpn. J. Appl. Phys.*, 28 (1989) L1800.
- 11 H. Zama, J. Saga, T. Hattori and S. Oda, *Jpn. J. Appl. Phys.*, 33 (1994) L312.
- 12 K. Zhang, B. S. Kwak, E. P. Boyd, A. C. Wright and A. Erbil, *Appl. Phys. Lett.*, 54 (1989) 380.
- 13 P. H. Dickinson, T. H. Geballe, A. Sanjurjo, D. Hildenbrand, G. Craig, M. Zisk, J. Collman, S. A. Banning and R. E. Sievers, *J. Appl. Phys.*, 66 (1989) 444.
- 14 J. Zhao, K.-H. Dahmen, H. O. Marcy, L. M. Tonge, T. J. Marks, B. W. Wessels and C. R. Kannewurf, *Appl. Phys. Lett.*, 53 (1988) 1750.
- 15 A. J. Panson, R. G. Charles, D. N. Schmidt, J. R. Szedon, G. J. Machiko and A. I. Braginski, *Appl. Phys. Lett.*, 53 (1988) 1756.
- 16 M. A. Subramanian, C. C. Torardi, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdry and A. W. Sleight, *Science*, 239 (1988) 1015.
- 17 P. Majewski, B. Hettich, H. Jaeger and K. Schulze, *Adv. Mater.*, 3 (1991) 1.
- 18 J. M. Zhang, H. O. Marcy, L. M. Tonge, B. W. Wessels, T. J. Marks and C. R. Kannewurf, *Appl. Phys. Lett.*, 55 (1989) 1906.
- 19 S. Ghoda and Y. Maeda in *MRS Symp. Proc.* 169, Eds. D. Christen, J. Narayan and L. Schneemeyer, MRS, Pittsburgh 1990, p. 611.
- 20 M. Nemoto and M. Yamanaka, *J. Mater. Res.*, 5 (1990) 1.
- 21 N. Hamaguchi, J. Vigil, R. Gardiner and P. S. Kirlin, *Jpn. J. Appl. Phys.*, 29 (1990) L596.
- 22 J. Zhang, J. Zhao, H. O. Marcy, L. M. Tonge, B. W. Wessels, T. J. Marks and C. R. Kannewurf, *Appl. Phys. Lett.*, 54 (1989) 1166.
- 23 T. Kimura, H. Nakao, H. Yamawaki, M. Ihara and M. Ozeki, *IEEE Trans. Magn.*, 27 (1991) 1211.
- 24 A. Hårsta in *Superconductivity and Superconducting Mater. Technol.*, Adv. Sci. Technol. Vol. 8, Ed. P. Vincenzini, Techna Srl., Faenza, Italy, 1995, p. 549.
- 25 M. Ottosson, A. Hårsta and J.-O. Carlsson, *J. Crystal Growth*, 96 (1989) 1019.
- 26 A. Hårsta and J.-O. Carlsson, *J. Crystal Growth*, 98 (1989) 561.
- 27 A. Hårsta and J.-O. Carlsson, *J. Less-Common Met.*, 164/165 (1990) 716.
- 28 M. Ottosson, A. Hårsta and J.-O. Carlsson, *J. Electrochem. Soc.*, 138 (1991) 778.
- 29 A. Hårsta and J.-O. Carlsson, *J. Crystal Growth*, 110 (1991) 631.
- 30 A. Hårsta and J.-O. Carlsson, *J. Crystal Growth*, 114 (1991) 507.
- 31 C. Vahlas and T. M. Besmann, in *Chem. Vap. Dep.*, 11th Int. Conf., Eds. K. E. Spear and G. W. Cullen, The Electrochem. Soc., Pennington, N. J., 1990, p. 188.
- 32 C. Vahlas and T. M. Besmann, *J. Am. Ceram. Soc.*, 75 (1992) 2679.
- 33 A. Pisch, F. Weiss and C. Bernard, *Physica, C* 235-240 (1994) 309.
- 34 F. Weiss, A. Pisch, C. Bernard and U. Schmatz, *J. de Physique IV* 5 (1995) C5-151.
- 35 N. I. Ilyinyh, G. K. Moiseev, N. A. Vatolin and J. Šesták, *Thermochim. Acta*, 198 (1992) 357.
- 36 Y. K. Rao and S. S. Kim, *J. Supercond.*, 2 (1989) 395.
- 37 B. Nöläng, Thesis, Acta Univ. Ups. (Fac. Sci.), 691 (1983).
- 38 F. van Zeggeren and S. H. Storey, *The Computation of Chemical Equilibria*, Cambridge University, Cambridge, 1970.
- 39 W. R. Smith and R. W. Missen, *Chemical Reaction Analysis*, Wiley-Interscience, New York, 1982.
- 40 K. Kanehori, N. Sugii, T. Fukuzawa and K. Miyauchi, *Thin Solid Films*, 182 (1989) 265.
- 41 J. Zhao, C. S. Chern, Y. Q. Li, P. Norris, B. Gallois, B. Kear, X. D. Wu and R. E. Muenchausen, *Appl. Phys. Lett.*, 58 (1991) 2839.
- 42 J. M. Zhang, B. W. Wessels, L. M. Tonge and T. J. Marks, *Appl. Phys. Lett.*, 56 (1990) 976.
- 43 J. M. Zhang, B. W. Wessels, D. S. Richeson and T. J. Marks, *J. Crystal Growth*, 107 (1991) 705.