THERMODYNAMIC MODELING OF MOCVD OF THE SUPERCONDUCTING PHASE IN THE Bi-Sr-Ca-Cu-O SYSTEM : INFLUENCE OF METAL PRECURSOR AND OXYGEN SOURCE

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Abstract - Chemical vapour deposition (CVD) of the superconducting 2:2:1:2 phase in the Bi-Sr-Ca-Cu-O system from different metalorganic precursors is thermodynamically investigated. Both precursors without fluorine and fluorine-containing precursors were employed. The oxygen source was O_2 , H_2O , O_2+H_2O or N_2O . The effect of different deposition parameters on the extension of the region where the 2:2:1:2 phase can be deposited is studied, and the results are presented in calculated CVD stability diagrams. For precursors containing no fluorine, the best conditions were obtained by using N_2O as the oxygen source and by using a low total pressure. For fluorine-containing precursors, the best conditions were obtained using a mixture of O_2 and H_2O as the oxygen source. Moreover, the size of the region where the 2:2:1:2 phase can be deposited is reduced compared to when precursors without fluorine are used. The results of the thermodynamic calculations are found to agree well with experimental results.

1. INTRODUCTION

The Bi-Sr-Ca-Cu-O system contains several superconducting phases, e. g. the $Bi_2Sr_2CaCu_2O_{8+x}$ phase (2:2:1:2) with $T_c \approx 85$ K and the $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ phase (2:2:2:3) with $T_c \approx 110$ K. A promising method to produce these high- T_c superconductors is chemical vapour deposition (CVD). This technique has many advantages such as that the oxygen activity can be controlled during growth, the microstructure and texture can be controlled and superconducting films can be obtained *in situ*. The most common precursors in CVD of the superconducting phases in the Bi-Sr-Ca-Cu-O system have been various metalorganic compounds [1-17].

Several different metalorganic compounds have been employed as metal precursors. For the elements Sr, Ca and Cu, metal chelates are exclusively used. They have the general formula $R_1-CO-CH-CO-R_2$, where R_1 and R_2 denote either an alkyl group or a fluorosubstituted alkyl group. The following metal chelates have been used:

- (1) $R_1 = R_2 = CH_3$, acetylacetonate, denoted **a**;
- (2) $R_1 = R_2 = C(CH_3)_3$, dipivaloylmethanate, denoted **d**;
- (3) $R_1 = C(CH_3)_3$, $R_2 = CF_2CF_2CF_3$, heptafluorodimethyloctanedionate, denoted **f**;
- (4) $R_1 = R_2 = CF_3$, hexafluoropentanedionate, denoted **h**.

For the element Bi, the following two compounds have been employed:

- (5) $Bi(OC_2H_5)_3$, bismuth triethoxide, where the ligand is denoted **e**;
- (6) $(C_6H_5)_3Bi$, triphenyl bismuth, where the ligand is denoted **t**.

Furthermore, different oxygen sources such as O_2 , O_2+H_2O and N_2O have been used. In table 1, data on the metal precursors and oxygen sources used have been compiled for the CVD experiments made in the Bi-Sr-Ca-Cu-O system. Also the deposition temperature, the total pressure and the possible formation of the superconductor without post-annealing are given. It can be seen that a deposition temperature of at least $750^\circ C$ is required to obtain the superconducting phase *in situ*.

Table 1. Preparation of thin films of the superconducting phase in the Bi-Sr-Ca-Cu-O system by MOCVD. The notations a, d, e, f, h and t for the different metal precursors are explained in the text.

Ref.	Metal precursor				O_2 -source	T($^\circ C$)	p(kPa)	<i>in situ</i>
	Bi	Sr	Ca	Cu				
/1/	t	d	d	a	O_2	500	100	No
/2/	e	d	d	d	O_2	910	0.133	Yes
/3/	t	d	d	a	O_2+H_2O	550	0.267	No
/4/	e	d	d	d	O_2	770	0.133	No
/5/	e	d	d	d	O_2	770-850	0.133	Yes
/6/	t	d	d	d	O_2	795-810	0.133	Yes
/7/	t	d	d	a	O_2+H_2O	550	0.267	No
/8/	t	d	d	d	O_2	650^a	0.001	No
/9/	t	d	d	d	O_2	650^a	0.001	No
/10/	t	h	h	h	O_2	600	2.66	No
	t	d	d	h	O_2	600	2.66	No
/11/	t	d	d	a	N_2O	625	0.33	No
/12/	t	d	d	d	O_2	750-800	6.67	Yes
/13/	t	f	f	h	O_2	500	0.27	No
/14/	t	d	d	d	O_2	850	1.33	Yes
/15/	t	d	d	d	O_2	$650-700^a$	0.08-0.11	No
/16/	t	d	d	a	O_2+H_2O	550-625	0.27	No
/17/	t	d	d	d	O_2	800-850	0.93	Yes

^a = Plasma-CVD

As mentioned earlier several superconducting phases exist in the Bi-Sr-Ca-Cu-O system. However, when preparing thin films by CVD, the majority phase obtained is invariably the 2:2:1:2 phase. This agrees well with the reported large thermodynamic stability of this phase /18/. Lead has been reported to promote the formation of the 2:2:2:3 phase and Zhang *et al.* /7, 16/ have prepared Pb-doped Bi-Sr-Ca-Cu-O films. However, the 2:2:1:2 phase constituted the majority phase also in these films, but an increased c-axis preferred orientation was reported. It may also be noted that a higher deposition temperature has been found to increase the amount of the 2:2:2:3 phase /17/.

One of the major obstacles in MOCVD of the superconducting high- T_c materials, is codeposition of carbonates and fluorides. This may severely affect the superconducting properties of the films. Such codeposition has been reported in MOCVD of the $YBa_2Cu_3O_{7-x}$ phase (see *e. g.* /19, 20/), and fluorine has also been reported to be incorporated in the films in MOCVD of the 2:2:1:2 phase /10, 13/. This contamination was, however, removed during the annealing process. It has also been reported that all four metal components cannot be deposited by using water as the only oxygen source /3/, but that the presence of oxygen is necessary to deposit bismuth.

In earlier investigations, thermodynamic modeling of CVD of the superconducting phases in the Y-Ba-Cu-O system from both halide /21, 22/ and metalorganic /23/ precursors and in the Bi-Sr-Ca-Cu-O system from halide precursors /24, 25/ has been presented. The effect of varying different deposition parameters was studied and the results were presented in calculated CVD stability diagrams. The results were found to agree well with the experimental studies. In the present paper, the developed methodology is applied on CVD of the 2:2:1:2 phase in the Bi-Sr-Ca-Cu-O system from metalorganic precursors. Special emphasis is put on the possible formation of carbonates and fluorides. The effect of employing different oxygen sources (O_2 , H_2O , O_2+H_2O and N_2O) is also thermodynamically investigated.

2. THERMODYNAMIC CALCULATIONS

In CVD of the superconducting 2:2:1:2 phase in the Bi-Sr-Ca-Cu-O system, *i. e.*, a compound consisting of five elements, many degrees of freedom exist. First suitable source materials for the components have to be selected. In the present thermodynamic calculations, the following combinations of compounds were chosen as metal precursors. These combinations have all been used in CVD of the 2:2:1:2 phase:

- (1) $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(a)_2$;
- (2) $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(d)_2$;
- (3) $Bi(t)_3$, $Sr(h)_2$, $Ca(h)_2$ and $Cu(h)_2$.

The notations **a**, **d**, **h** and **t** for the ligands are explained in the introduction. Also the oxygen sources were chosen to be the compounds that have been used in experimental work, *i. e.*, O_2 , O_2+H_2O and N_2O . In addition to these sources, calculations were also made for H_2O as oxygen source. Other variables include the deposition temperature, the total pressure and the inlet partial pressure of the gaseous precursors. For such a multi-component system, thermodynamics can be used as a guide to predict the deposition conditions /21-25/. The results of the thermodynamic calculations are summarized in calculated CVD stability diagrams.

The free-energy minimisation technique (computer program EKVICALC /26/) was used in all calculations. In the CVD stability diagrams, the input ratio $Bi(t)_3:Sr(X)_2:Ca(Y)_2:Cu(Z)_2$ ($X = d$ or h , $Y = d$ or h , $Z = a, d$ or h) was fixed to 2:2:1:2 as in the earlier calculations /24, 25/. This ratio is supported by the stoichiometry of the 2:2:1:2 phase and the nearly quantitative yield of the binary oxides upon deposition. Four different oxygen-containing vapours were attempted, O_2 , H_2O , O_2+H_2O and N_2O . The calculations were repeated for different temperatures, pressures and ratios between the oxygen sources and the metal precursors. The yield of a binary oxide is defined as the amount of oxide obtained in the calculations divided by the input amount of the metalorganic compound. About 140 substances were included in the thermodynamic calculations.

No ternary or quaternary oxides were included in the calculations, since no thermodynamical data have been reported for these phases. Furthermore, no thermodynamical data exist for the superconducting 2:2:1:2 phase. However, the largest gain in free-energy occurs when the binary oxides are formed. Rather small decreases in free-energy are to be 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 are deposited, are thus regarded to be the regions in which the 2:2:1:2 phase can be deposited. This is supported by the results from thermodynamic calculations for the Y-Ba-Cu-O system /21/. In this system thermodynamic data has been reported for the superconducting phase. It was found that the position and size of the regions where the superconducting phase 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. The sizes of these regions were, however, found to be considerably smaller.

It should also be observed that no thermodynamic data exist for the metalorganic compounds. 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. This will not affect the CVD stability diagrams, since they only reflect the final state of the system at equilibria. The driving force values for the reactions are affected, but these quantities are not considered in the present work.

3. RESULTS AND DISCUSSION

As mentioned previously, the regions in the CVD stability diagram, where only the four binary oxides are deposited, are considered to be the regions of interest in the following. This region is called "2:2:1:2" in the following and has been denoted by a gray shade in figs. 1-2. The remaining regions in the CVD stability diagrams and the phases present in these regions have not been indicated. Furthermore, some calculated CVD stability diagrams have been omitted due to space limitations. The sum $[Bi(t)_3] + [Sr(X)_2] + [Ca(Y)_2] + [Cu(Z)_2]$ where $X = d$ or h , $Y = d$ or h , $Z = a$, d or h , is denoted ΣM in the following discussion.

In the CVD stability diagrams of figs. 1-2, the yield of the binary oxides has not been indicated. However, both SrO and CaO are invariably deposited with a yield of 100% and the yield of CuO/Cu₂O always exceeds 80%. The lowest and limiting yield is thus the yield of Bi₂O₃. This yield is 100% at lower temperatures but falls off towards the upper part of the "2:2:1:2" region.

3. 1. The influence of the carbon/hydrogen ratio

Fig.1. Calculated CVD stability diagrams for the $Bi(t)_3$ - $Sr(d)_2$ - $Ca(d)_2$ - $Cu(d)_2$ - O_2 (tddd) and $Bi(t)_3$ - $Sr(d)_2$ - $Ca(d)_2$ - $Cu(a)_2$ - O_2 (tdda) systems.

The calculations have been summarized in fig. 1. All calculations were made using O_2 as the oxygen source and at a total pressure of 1 kPa. Two different conditions were considered, either using $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(d)_2$ or using $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(a)_2$ as metal precursors. In the first case, the carbon/hydrogen ratio is 0.664 and in the second case 0.709. As can be seen from table 1, both these cases have been employed in experimental work.

In order to obtain a "2:2:1:2" region, a rather high deposition temperature has to be used. Below this temperature, no SrO can be formed and $SrCO_3$ is instead deposited. This temperature can be reduced by using a higher $[O_2]/\Sigma M$ ratio. For the metal precursors $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(d)_2$ and a $[O_2]/\Sigma M$ ratio of 2, a deposition temperature of 840°C is needed, while for a $[O_2]/\Sigma M$ ratio of 5 this temperature can be reduced to 610°C. The effects of changing the metal precursors from $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$, $Cu(d)_2$ to $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$, $Cu(a)_2$, i. e., to increase the carbon/hydrogen ratio, are rather small. The size of the "2:2:1:2" region is, however, somewhat expanded towards a lower temperature (with about 10°C).

3. 2. The influence of the total pressure

These calculations were made for three different pressures, 0.1, 1 and 10 kPa. All calculations were made using O_2 as the oxygen source and with $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(a)_2$ as metal precursors.

The position of the "2:2:1:2" region is shifted towards a lower temperature when the total pressure is decreased. Below this region, $SrCO_3$ is deposited instead of SrO . For a total pressure of 0.1 kPa and a $[O_2]/\Sigma M$ ratio of 3, a deposition temperature of 670°C is needed to obtain a "2:2:1:2" region. In contrast, for a total pressure of 10 kPa and with the same $[O_2]/\Sigma M$ ratio, this temperature is increased to 840°C. It should be noted that for the lowest pressure, 0.1 kPa, no Bi_2O_3 can be deposited at high temperatures and high $[O_2]/\Sigma M$ ratios.

3. 3. The influence of the oxygen source

These calculations were made for three different oxygen sources, O_2 , H_2O and N_2O . All calculations were made at a total pressure of 1 kPa and with $Bi(t)_3$, $Sr(d)_2$, $Ca(d)_2$ and $Cu(a)_2$ as metal precursors.

When H_2O is used as the oxygen source no "2:2:1:2" region can be obtained. Neither CuO/Cu_2O nor Bi_2O_3 can be deposited in any parts of the composition and temperature range investigated. In contrast, using either O_2 or N_2O as the oxygen source a "2:2:1:2" region is obtained. Below this region, $SrCO_3$ is deposited instead of SrO . The position of the "2:2:1:2" region is somewhat shifted towards a lower temperature when N_2O is employed. For a $[N_2O]/\Sigma M$ ratio of 3, a deposition temperature of 725°C is needed to obtain a "2:2:1:2" region. Using O_2 as the oxygen source and for a $[O_2]/\Sigma M$ ratio of 3, this temperature is increased to 745°C.

3. 4. Fluorine containing precursors

The calculations are summarized in fig. 2. All calculations were made at a total pressure of 1 kPa with $Bi(t)_3$, $Sr(h)_2$, $Ca(h)_2$ and $Cu(h)_2$ as metal precursors. Three different oxygen sources were employed, O_2 , O_2+H_2O and H_2O . When the O_2+H_2O mixture was used, the ratio $[O_2]/[H_2O]$ was fixed to 1/1. Only this latter CVD stability diagram is shown in fig. 2.

A "2:2:1:2" region is only obtained when a mixture of O_2 and H_2O is used as the oxygen source. This region is rather small and high temperatures and high values of the $([O_2]+[H_2O])/ \Sigma M$ ratio is necessary. Fluorine-containing precursors seem to prevent the formation of $SrCO_3$ and $CaCO_3$, since these carbonates do not exist in any region in the three CVD stability diagrams. However, SrF_2 occurs in large parts of the diagrams. When O_2 is used as the oxygen source, SrF_2 is present in all parts of the CVD stability diagram. In contrast, with H_2O as the oxygen source, a small region exists at high temperatures and high $[H_2O]/\Sigma M$ ratios where no SrF_2 is deposited. However, no CuO/Cu_2O or Bi_2O_3 can be deposited in any parts of the CVD stability diagram using only H_2O as the oxygen source.

Fig. 2. Calculated CVD stability diagram for the $\text{Bi}(\text{t})_3\text{-Sr}(\text{h})_2\text{-Ca}(\text{h})_2\text{-Cu}(\text{h})_2\text{-O}_2\text{-H}_2\text{O}$ system.

4. SUMMARY AND CONCLUDING REMARKS

Chemical vapour deposition of the superconducting 2:2:1:2 phase in the Bi-Sr-Ca-Cu-O system from metalorganic precursors has been investigated thermodynamically. The results are summarized in calculated CVD stability diagrams. It should be emphasized that these diagrams should only be used as a guide to how the deposition conditions are affected, when the deposition parameters are varied. The most important points are the following.

For precursors without fluorine, a "2:2:1:2" region is obtained at the lowest temperature when O_2 is replaced by N_2O as the oxygen source. A low deposition temperature is, furthermore, favoured by a decreased total pressure and by using a precursor with a higher carbon/hydrogen ratio. The effect of the latter is, however, rather small. No "2:2:1:2" region can be obtained when H_2O is employed as the oxygen source.

For fluorine-containing precursors, a "2:2:1:2" region can only be obtained if O_2 is replaced by an $\text{O}_2+\text{H}_2\text{O}$ mixture as the oxygen source. The size of this region is, however, considerably smaller than the corresponding size for precursors without fluorine. Finally, no "2:2:1:2" region can be obtained using exclusively H_2O as the oxygen source.

The results of the thermodynamic calculations agree well with the experimental observations. A rather high temperature ($\approx 750^\circ\text{C}$) has been reported to be required for deposition of the 2:2:1:2 phase *in situ* (see table 1). Furthermore, the presence of O_2 is necessary, i. e., no 2:2:1:2 phase can be deposited using only H_2O as the oxygen source /3/. The thermodynamic calculations predict that N_2O should be the best oxygen source. This has also been reported in CVD of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase /27/, but in the only existing investigation in the Bi-Sr-Ca-Cu-O system using N_2O as the oxygen source /11/, the deposition temperature was probably too low to obtain the 2:2:1:2 phase *in situ* (see table 1). Using fluorine-containing precursors, no 2:2:1:2 phase has been obtained without post-annealing of the deposited layers /10, 13/. According to the results from 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.

It is interesting to compare the results of the present calculations to the results of thermodynamic calculations for CVD of the superconducting 2:2:1:2 phase from halide precursors /24, 25/. In these calculations, a large size of the "2:2:1:2" region was favoured by a high total pressure. This is in contrast to the present findings for metalorganic precursors. Furthermore, in the halide systems, the oxygen source yielding the best deposition conditions, was found to be $\text{O}_2+\text{H}_2\text{O}$ for

metal chloride precursors and O_2 for metal iodide precursors. In contradiction to the results for metalorganic precursors, the CVD stability diagrams were not affected when O_2 was replaced by N_2O as the oxygen source in the halide systems.

A comparison of the present results with the results of thermodynamic calculations for CVD of the superconducting $YBa_2Cu_3O_{7-x}$ from metal chelate precursors [23] is also interesting. All results regarding trends when the deposition conditions are changed are essentially the same. In both investigations, the best results are obtained by using N_2O as the oxygen source, a low total pressure and a high carbon/hydrogen ratio. Furthermore, if fluorine-containing precursors are used, a mixture of H_2O and O_2 is necessary in order to deposit the superconducting phases. Moreover, the sizes of the regions where the superconducting phases can be deposited are considerably reduced compared to the corresponding sizes when precursors without fluorine are used.

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