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HIGH-TC-SUPERCONDUCTORS PREPARED BY CVD

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Abstract:

YBa₂Cu₃O_{7- δ} deposition experiments were carried out in a cold wall stagnation flow CVD-reactor on single crystalline (100)-oriented SrTiO₃-substrates at a total pressure of 10 mbar. As source materials different β -diketonate derivatives of yttrium, barium and copper were investigated concerning their volatility and decomposition behaviour. Finally for the YBa₂Cu₃O_{7- δ} deposition process Y(thd)₃, Ba(thd)₂ and Cu(thd)₂ were used. The evaporation temperatures T_v were 112, 208 and 117 °C respectively. High quality films can be obtained with the c-axis perpendicular to the substrate surface at temperatures higher than 850 °C. The transition temperatures of the coatings are higher than 90 K and the critical current densities are in the order of $j_c = 10^6$ A/cm² at 77 K and self magnetic field.

Introduction:

Suitable production methods of High-T_c-superconducting thin films for electronic (e.g. SQUID's, microwave-devices, integrated circuits) and electrotechnical (e.g. cables, magnets, current limiters, transformers, storage devices) applications in the most cases require the deposition on large areas. The deposited films should be uniform in thickness and composition and the growth rates should satisfy industrial demands. For electrotechnical applications normally thick superconducting layers ($d_s > 1 \mu\text{m}$) are necessary in order to obtain a large superconducting cross-section leading to a high current carrying ability. This means that, due to the anisotropic properties of the oxide superconductors, epitaxial grain growth with layers thicker than 1 μm are required. Chemical vapour deposition satisfies this requirement due to the molecular nature of the deposition process. Furthermore, it is well known, that in the case of complicated shaped substrate geometries (e.g. fibres), CVD seems to be the only technique, compared to all physical vapour deposition techniques and wet chemical procedures, to realize these demands. Meanwhile these potential of CVD has been recognized by an increasing number of scientists at the universities as well as in the industrial laboratories /1/. However, the main problem in the development of the CVD-process for High-T_c-superconductors till now is the availability of suitable source materials with acceptable physical and chemical properties.

This paper describes investigations on possible source materials concerning their usability for the CVD-process of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposition. The CVD-equipment which has been used for the deposition process, the deposition kinetics and the superconducting properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ coatings are described.

Source materials:

Each CVD-process requires suitable precursors carrying the elements, which have to be deposited via the vapour phase onto the hot substrate material. The demands on such precursors are manifold. They should have to be thermally stable and have high vapour pressures at moderate temperatures up to 300 °C but they should decompose at temperatures higher than 500 °C without the formation of stable residuals during their pyrolysis. The precursors currently used for the deposition of High- T_c -superconductors in the YBaCuO-system are mainly β -diketonate derivatives which are well known to form volatile metal-compounds /2/3/. Only a few results are known concerning the application of halides /4/. Tab. 1 summarizes some possible β -diketonates of yttrium, barium and copper.

R1	R2	Short Name
CH ₃	CH ₃	M(acac) _n
t-C ₄ H ₉	t-C ₄ H ₉	M(thd) _n M(dpm) _n
CF ₃	CF ₃	M(hfac) _n
n-C ₃ F ₇	t-C ₄ H ₉	M(fod) _n

Table 1: Source materials, with: acac: acetylacetone or 2.4-pentanedione; hfac = hexafluoroacetylacetone or 1.1.1.5.5.5-hexafluoropentane-2.4-dione; thd = 2.2.6.6-tetramethylheptane-3.5-dione or dpm = dipivaloylmethane and fod = 1.1.1.2.2.3.3-heptafluoro-7.7-dimethyloctane-4.6-dione.

The results of evaporation experiments in the CVD-arrangement /5/6/ are shown in fig. 1, where the molar evaporation rates $\dot{n}_{ev}$ of the investigated compounds are plotted in a logarithmic scale versus the reciprocal evaporation temperature T_v . The experiments were carried out at a total pressure of $p_{tot} = 10$ mbar and a carrier gas flow of 50 l/h Argon (STP). The geometry of the evaporation crucibles is described in more detail in /7/. The evaporation rates $\dot{n}_{ev}$ were determined by measuring the weight change of the powder after the experiments.

Fig. 1: Molar evaporation rates $\dot{n}_{ev}$ of $Y(thd)_3$, $Ba(thd)_2$ with and without $H(thd)$, $Ba(fod)_2$, $Cu(acac)_2$, $Cu(thd)_2$ and $Cu(hfac)_2$ versus the reciprocal evaporation temperature T_v .

In the case of copper we have investigated $Cu(acac)_2$, $Cu(hfac)_2$ and $Cu(thd)_3$. The evaporation behaviour of these compounds is very different. The volatility increases in the sequence $Cu(acac)_2 < Cu(thd)_2 < Cu(hfac)_2$ mainly caused by the different ligands, which influence the van-der-Waal's interactions between adjacent molecules. Pyrolysis of these compounds in oxygen containing atmosphere at temperatures $T > 500^\circ C$ leads in every case to monoclinic CuO /5/. In the case of Yttrium only $Y(thd)_3$ has been investigated. The evaporation behaviour is very similar to that observed with $Cu(thd)_2$ but shifted to higher temperatures. Thermal decomposition leads to stoichiometric Y_2O_3 /5/. In the case of Barium precursors three compounds have been investigated: $Ba(acac)_2$, $Ba(fod)_2$ and $Ba(thd)_2$. $Ba(acac)_2$ is not usable for a CVD-process because it already dissociates in the crucible and only the volatile organic parts of the molecules leave the evaporator. $Ba(fod)_2$ shows a rather good volatility at temperatures below $200^\circ C$. The main disadvantage of this compound is, that it decomposes on the hot substrate to BaF_2 which is thermodynamically exceptionally stable /8/ and can only be converted to the corresponding oxide by an additional heat treatment in a water-containing atmosphere /9/. $Ba(thd)_2$ has the advantage of fluorine free decomposition products (BaO with small amounts of $BaCO_3$) /5/ although high temperatures ($T_v > 200^\circ C$) are necessary in order to obtain suitable evaporation rates ($\dot{n}_{ev} > 10^{-6}$ mol/min). The disadvantage of this compound, compared to the yttrium- and copper-chelates, is, however, a strong tendency to form oligomers during the evaporation process. The reason for this behaviour is the unsaturated coordination sphere of Barium. The $Cu(II)$ -ion in $Cu(acac)_2$ /10/11/ as well as in $Cu(thd)_2$ /12/ is surrounded by four oxygen atoms forming a planar square. Yttrium is surrounded by six oxygen atoms forming an octahedral coordination sphere as electron diffraction investigations in the vapour phase by S. Shibata et al. /13/ have shown. Therefore the Cu-chelates as well as $Y(thd)_3$ are expected to exist as monomeric molecules. However, the coordination sphere of the barium ion is unsaturated by the four oxygen atoms of the two chelate ligands. Higher coordination numbers can be attained by adding solvents or by oligomerization /14/. This behaviour of $Ba(thd)_2$ compared to $Y(thd)_3$ and $Cu(thd)_2$ was clearly observed doing evaporation experiments in a microbalance. The set-up of the arrangement is described in /7/. The evaporation conditions in the microbalance were similar to those in the CVD-equipment.

Only the geometry of the crucible was different. As carrier gas we used Ar+O₂ (1:1) at a total pressure of 10 mbar. All compounds showed some instabilities during the heating-up period (30 min) due to the additional evaporation of residuals of water, solvents or free ligands. After this heating-up period the evaporation of Y(thd)₃ and Cu(thd)₂ became stable within the investigated period of time (10 h). Ba(thd)₂, however, showed constant evaporation rates only if the evaporation temperature was in the range of 200 °C or below (depending on the supplier). At higher temperatures (200 °C < T_v < 250 °C) the decrease of the evaporation rates of Ba(thd)₂ with time becomes more significant /7/. AAS-analysis (atomic absorption spectroscopy) of the Ba(thd)₂-precursor before and after the experiment at T_v = 220 °C showed an increase of the Ba-content from 26.3 ± 0.03 % in the initial material (theoretical value is 27.25 %) to 35.7 % in the residual substance. This indicates, that the main reason for the gradual decrease of the evaporation rates of Ba(thd)₂ must be partly decomposition or the strong interaction between the molecules, due to the unsaturated coordination sphere of Ba, which leads to an oligomerization to higher units. This effect significantly increases with increasing temperature. To overcome this some groups have tried to add donor ligands occupying free coordination sites. We have found /5/7/, as was also proposed by P.H. Dickinson et al. /15/, that adding H(thd) (2.2.6.6-tetramethyl-3.5-heptanedionate) to the carrier gas, the transport rates of Ba(thd)₂ can be stabilized with time at temperatures T_v < 220 °C, and in addition, the temperature dependence of the evaporation rate decreases (fig. 1, Ba(thd)₂ × L), corresponding to a lower activation energy. Other possibilities have been shown by S. Matsumo et al. /16/ adding THF (tetrahydrofuran) and recently by C.F. Barron /17/ who added nitrogen containing gases such as ammonia or amines (e.g. NEt₃) to Ba-β-diketonates instead of an oxygen donor, resulting in a depression of the melting point of Ba(thd)₂ (70 - 100 °C) and constant vapour pressures. The TNO group /18/ synthesized Ba(hfac)₂-tetraglyme [Barium bis (1.1.1.5.5.5.-hexafluoropentane-2.4-dionate) 2.5.8.11.14-pentaoxapentadecane], a fluorinated complex which is air-stable and exhibits a high stability of evaporation rate even after prolonged time. However, decomposition experiments with this complex under usual CVD-conditions also resulted in the formation of BaF₂ /19/. For example the preparation of the HT_c-superconductor Bi-Sr-Ca-Cu-O by J.M. Zhang et al. /20/ using these fluorinated compounds also resulted in films with fluoride phases showing semiconducting behaviour in a first step before posttreating the films in an oxygen-containing atmosphere at 650 °C and 865 °C. To avoid the problems caused by the (thd)-system Th. Kruck and coworkers /21/ proposed the use of real organometallic precursors such as (η⁸-cyclooctatetraenyl) (η⁵-cyclopentadienyl) yttrium ((COT) (Cp*)Y), bis (η⁵-pentamethylcyclopentadienyl) barium (Cp*₂Ba) and (η⁵-cyclopentadienyl)-(triethylphosphine) copper (Cp(PEt₃)Cu), which should have similar evaporation temperatures (below 200 °C) with no formation of associates. However, no results concerning the evaporation behaviour of these compounds and their decomposition kinetics are available till now.

For our YBa₂Cu₃O_{7-δ} deposition experiments we chose Y(thd)₃, Ba(thd)₂ and Cu(thd)₂ as source materials due to their similar evaporation behaviour and moreover in order to avoid fluoride formation in the coating.

Desposition experiments:

Fig. 2 shows a schematic diagram of the CVD arrangement used for the deposition experiments of YBa₂Cu₃O_{7-δ} on flat substrates. The equipment mainly consists of three parts: the gas supply, the evaporators and the reactor. The evaporators, made from stainless steel, are electrically heated independently from each other due to the different evaporation behaviour of the source materials in order to control the stoichiometry of the coatings. The evaporation temperatures T_v are measured directly in the powder by a NiCr/Ni thermocouple. The temperatures T_{v1,2,3} which are necessary for a 1:2:3 stoichiometry of Y(thd)₃, Ba(thd)₂ and Cu(thd)₂ in the vapour phase are, as an example indicated in fig. 1. Like in most cases /1/ the

gaseous evaporated compounds are transported with the help of a carrier gas (18 l/h oxygen (STP) for each evaporator and in addition 40 l/h argon (STP) which was enriched with H(thd) by bubbling through the co-evaporator for Ba(thd)₂) into the CVD-reactor. Only few results are known concerning the evaporation of the source materials without carrier gas /22/23/ or by introducing the solid precursors directly into the CVD-reactor e.g. with the help of a powder feeder /24/. The vertical reactor (ϕ 50 mm) is a cold-wall type with a stagnation flow arrangement. The substrate holder, made by an Ni-based alloy (Nimonic), is heated inductively using an RF-Generator (200 KHz, 2,5 kW). The temperature T_s of the substrate holder is measured by a NiCr/Ni - thermocouple inserted into the substrate holder on the backside of the sample. The temperature of the substrate surface is approximately 100 °C lower at $T_s = 950$ °C. To exclude the instability of the evaporation behaviour of the source materials during the heating-up period and in order to obtain defined deposition times, we have installed a thermostated by-pass line made from stainless steel, with two heated valves which allows to separate the gas flow from the CVD-reactor during the initial phase. The stagnation flow reactor, which has already been described in detail /5/25/26/ has the advantages, that reactions between the reactor wall and reactive species can be minimized and that a very homogeneous mass transport to the substrate surface can be obtained if suitable flow conditions are used.

Fig. 2: Schematic diagram of the CVD-arrangement

All deposition experiments were carried out at a total pressure of $p_{\text{tot}} = 10$ mbar. Typical deposition times were between 30-60 min. After the deposition experiment the reactor was filled up with pure oxygen to ambient pressure within 10 min and cooled down to room temperature with a cooling rate of 15 °C/min. As substrate material single crystalline (100)-oriented SrTiO₃ (1 cm²) was used due to its good lattice matching with the a-b-plane of YBa₂Cu₃O_{7- δ} providing the deposition of highly oriented layers.

Fig. 3 shows in a logarithmic scale the growth rates $\dot{s}$ of YBa₂Cu₃O_{7- δ} versus the reciprocal substrate holder temperature T_s . This curve is typical for a CVD-process. At low temperatures ($T_s < 600$ °C) the deposition of YBa₂Cu₃O_{7- δ} is temperature dependent with an activation

energy of $E_A = 82$ kJ/mol. In this region the deposition is controlled by the kinetics of the thermal decomposition of the source materials on the hot substrate surface forming $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This deposition range therefore should be favoured if complicated shaped deposition geometries have to be coated homogeneously. However, at these low temperatures ($T_s < 600$ °C) the surface mobility of adsorbed molecules is low and the supersaturation of the gas phase is high. Both leads to a high nucleation rate but low crystal growth rate and therefore to a fine-grained structure with poor superconducting properties. At temperatures higher than $T_s = 600$ °C the deposition rates of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ become independent of the substrate temperature T_s . In this region the deposition rates are limited by the mass transport of reactive species towards the substrate surface [27]. Maximum deposition rates obtained, under the conditions mentioned above, were 20 nm/min. These, however, can be increased by increasing the evaporation rates of the source materials. Depositions in the mass transport controlled range has the advantage that the deposition rates are high and moreover that the surface mobility increases with increasing temperature T_s . This provides, together with a low supersaturation suitable conditions for highly textured or even epitaxial coatings.

Fig. 3 : Growth rates $\dot{s}$ of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ versus the reciprocal abs. deposition temperature T_s

The composition of the coatings has been measured with the help of EDX-analysis within a rectangular area of 45×100 μm , by comparison (linear extrapolation) with a stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ standard. We have found, that in the mass transport controlled deposition range the composition of the coatings only slightly deviates from the composition of the vapour phase. However, in the temperature dependent deposition range the composition of the layer strongly deviates from the composition of the vapour phase. The deviations increase with decreasing temperature T_s . This effect can be explained by the different decomposition kinetics of the source materials [5/25] as shown in fig. 4, where the normalized deposition rates of the single oxides are plotted versus the reciprocal deposition temperature T_s . It can be seen, that the thermal decomposition of $\text{Y}(\text{thd})_3$ to Y_2O_3 is strongly temperature dependent at $T_s < 480$ °C with an activation energy of $E_A = 120$ kJ/mol. The decomposition of $\text{Cu}(\text{thd})_2$ is

temperature dependent at temperature $T_s < 530^\circ\text{C}$ with $E_A = 35\text{ kJ/mol}$. The Ba(thd)_2 decomposition, leading to a mixture of BaO and BaCO_3 , is kinetically controlled at $T < 800^\circ\text{C}$ with an activation energy ($E_A = 73\text{ kJ/mol}$) which is similar to the activation energy found for the simultaneous deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, but shifted to higher temperatures.

Fig. 4: Normalized deposition rates $\dot{s}$ of the single oxides Y_2O_3 , BaO/BaCO_3 and CuO versus the reciprocal absolute deposition temperature T_s

Results:

Fig. 5a shows a typical SEM-image of the surface morphology of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which has been deposited on single crystalline (100)-oriented SrTiO_3 substrates at $T_s = 950^\circ\text{C}$. EDX-analysis shows that the coating consist of a dense smooth $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -matrix into which Ba-free precipitates are inserted. These copper-yttrium-oxides are already formed during the initial growth process. The cross-section in fig. 5b clarifies that the precipitates range from the original substrate surface through the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -matrix to the top of the layer. This precipitates are mainly caused by instabilities in the vapour phase due to the strong temperature dependence of the evaporation process of the source materials (a deviation of 1°C results in a change of 10 % of the evaporation rate, fig. 1) and by the changing quality of the source materials from run to run. The deviation of the overall composition of the layer from the stoichiometry of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -phase can be characterized by a number ϵ , which is defined by the ratio of the number N_p of metal atoms in the precipitates and the total number N_t of metal atoms in the layer. N_t was calculated from the measured overall composition and N_p by comparison

Fig. 5: SEM-picture of the surface morphology (a) and cross-section (b) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on (100)-oriented SrTiO_3 -substrates

of N_t with the composition of the 123-phase. With ϵ , the total composition of the layer is given by:

$$\text{Y}_\alpha\text{Ba}_\beta\text{Cu}_\gamma\text{O} = (1-\epsilon) (\text{Y}_{1/6}\text{Ba}_{2/6}\text{Cu}_{3/6}\text{O}_{7-\delta}) + \epsilon (\text{Cu}_{1-z}\text{Y}_z\text{O}_n) \quad (\text{with } \alpha + \beta + \gamma = 1)$$

Therefore ϵ can be considered to be a measure of the surface density of precipitates and consequently of the roughness of the surface /5/28/.

Fig. 6 shows the X-ray pattern of a typical $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -coating with an ϵ of 0.05. The diagram shows a strong (00l)-orientation with the c-axis of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -unit cell perpendicular to the substrate surface. The maximum intensities are in the range of 10^6 cps. In addition the rocking curve, which is a measure for the degree of orientation, was obtained by measuring θ of the (007)-plane. It shows a FWHM (= full width at half maximum) of 0.35° which is comparable to coatings prepared by physical vapour deposition technologies /29/. The oxygen content in the coating, which was determined by calculating the length of the c-axis using the d-value of $(2\theta-\theta)$ of the (007)-reflex /30/, is between 6,9 - 7. Coatings with such a strong c-axis orientation show a temperature-resistance behaviour as indicated in fig. 7. The resistance decreases linearly with temperature, the transition temperature is in the range of $T_c = 90$ K. The critical current densities j_c of the coatings in zero field were usually measured in liquid nitrogen at 77.3 K, or in gaseous helium, if magnetic fields were applied. Before measuring, the samples had to be patterned by wet chemical etching in H_3PO_4 in order to reduce the absolute current and therefore the heat stress on the contacts. The widths of the current bridges were between 25 and 100 μm . The current and voltage contacts were made by sputtering Au pads onto the superconductor and connecting Ag wires with the help of Ag paste or metallic indium, which was pressed onto the Au pads. The critical current densities j_c of the measured samples, having layer thicknesses between 1 and 2 μm and $\epsilon < 0.4$, show j_c values in the range of 10^6 A/cm² at 77 K in self magnetic field. A systematic dependence of j_c on ϵ could not be found within the investigated range ($\epsilon < 0.4$).

Fig. 6: X-ray pattern of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on (100)-oriented SrTiO_3 and rocking curve

Fig. 7: Temperature-resistance behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on (100)-oriented SrTiO_3

Conclusion:

Chemical vapour deposition is a suitable method to deposit High- T_c -superconductors with good properties ($T_c > 90$ K, j_c (0T, 77) $> 10^6$ A/cm²) also on coatings having layer thicknesses larger than 1 μm . The most critical point till now is the quality of the precursors which often results in fluctuations of the evaporation rates and therefore in coatings with varying amounts of non-superconductive precipitates which reduce the superconducting cross-section.

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