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High-temperature chemical vapor deposition. An effective tool for the production of coatings*

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Abstract: Chemical vapor deposition (CVD) processes have a large throwing power and can operate at atmospheric pressure. Therefore, they are economical for many applications. High-temperature CVD processes give a good control of the crystal structure (e.g., epitaxial layers or other special layer structures) and support diffusion processes. The are used, for example, for the following deposition processes: 1) perovskites, 2) yttrium-stabilized ZrO_2 layers as ion conductors or heat barrier coatings, 3) aluminide diffusion coatings in long tubes for corrosion protection, and 4) BN on fibers for fiber-reinforced materials. The special properties of the perovskite CVD are discussed in more detail. These processes are described for small- and large-scale applications. The CVD process is simulated by the computer code Fluent.

INTRODUCTION

Depending on deposition conditions, a large spectrum of material structures (amorphous, polycrystalline, textured, epitaxial) can be obtained in nonequilibrium or near-equilibrium state. The last kind of coatings must be very often deposited at high temperatures in order to guarantee sufficient mobility of the atoms to come near to the equilibrium state. Examples of such coatings are yttrium-stabilized ZrO_2 (YSZ) and perovskite coatings [1]. Another reason for the necessity to use high-temperature chemical vapor deposition (HTCVD) processes is given, if the layer formation is connected with diffusion processes into the basic material. One example is thermochemical coatings (e.g., aluminizing of Ni-based alloys) [2]. Often, the kinetics of the process is only fast enough at a high temperature (e.g., BN coatings)[3].

This article will concentrate on the perovskite deposition. Among them

- ferroelectrics $BaTiO_3$, $Pb(Zr/Ti)O_3$ (= PZT)
- electrooptic and nonlinear optic materials ($LiTaO_3$, PZT, $Ti/LiNbO_3$)
- collossal magnetoresistive manganites, e.g., $(La,Pr)_{1-x}Ca_xMnO_3$
- electrodes for solid oxide fuel cells ($La_{1-x}Sr_xMO_3$ (M = Cr, Mn, Co))
- membrane materials with mixed conductivity, e.g., $La_{0.6}Sr_{0.4}Fe_{0,.2}Co_{0,8}O_{3-x}$ are of special importance.

Also, structurally related to perovskites are high-temperature superconductors $RBa_2Cu_3O_x$ (R = rare earth).

A number of important device applications are related to the properties mentioned. These devices are prepared in the form of mutilayered epitaxial heterostructures combining different structurally com-

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patible materials with different specific properties. Insulating barriers, protective coatings, Josephson effect devices, spin-polarized quasiparticle injection devices, interconnection and passive low-resistance components, and tunable filters can thus be realized. All of these applications are small-scale devices. Otherwise, the superconductors for superconducting cables demand deposited layers in a large scale (e.g., for cables).

CVD process development for perovskites has two interesting directions:

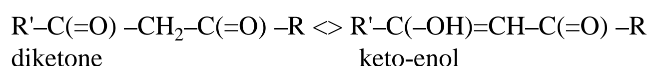
- methods to produce multilayer structures (e.g., by injection pulsed CVD [4]) and
- development of large-scale continuous deposition equipments (e.g., tape deposition [5]).

The interest in CVD of perovskites began with the discovery of the high T_c superconductors and the first deposition of this material by CVD [6]. In between, a large number of articles and review papers appeared about this area [7–9].

The description of the CVD of these materials is also interesting from a more general point of view: deposition of materials containing alkaline and alkaline earth elements needs a special precursor design because of the low volatility of the most of their compounds. On the other hand, the multicomponent materials containing up to five different cations are a challenge to the large-scale processes necessary for many applications. Mainly chelate compounds and in particular β-diketonates are used for the deposition of perovskites. We need first to discuss the peculiarities of CVD with chelate compounds.

PRECURSORS

As precursors for CVD processes, normally halogenides, hydrides, and alcoholates are used [10]. These precursors, however, are not suitable for rare-earth elements and for the elements of the I. and II. groups of the periodic system, which are necessary components of most perovskites, as well as the high T_c superconductors. These elements are very electropositive, and, therefore, they have the tendency to form strong ionic bonds. Consequently, compounds with these elements often have low vapor pressures. To obtain molecules with a high vapor pressure it is necessary to shield the Coulomb interaction of the metal in the compound. Since the work of Yamane [6], chelate compounds are the main candidates for such compounds. The chelates are formed by the β diketones, which exist in two tautomeres, the diketone and the keto-enol form:



R'–C(=O) –CH_2–C(=O) –R <> R'–C(–OH)=CH–C(=O) –R
diketone keto-enol

R and R' are organic radicals. The vapor pressure and the evaporation rate of these compounds are complex functions of the radius of the metal ion, the ionicity of the metal–oxygen bonds, the size of the ligands, and the nature of the organic radicals (e.g., introduction of F instead of H increases volatily drastically) with all the factors controlling the tendency to form less volatile associates [11]. Normally, thd compounds (2,2,6,6 tetramethyl hepta 3,5 dionate) with bulky organic radicals are used. Nevertheless, $Ba(thd)_2$ has a strong tendency to form associates because of the large ionic radius and the large coordination number of c = 8. The result of the association is the strong dependence of the composition and volatility on the method of synthesis. In the case of not waterfree method oligomeric water or hydroxyl containing compounds are formed: e.g., $Ba_5(thd)_9H_2O)_3(OH)$, $Ba_5(thd)_9ClH_2O)_7$ [12,13], $Ba_6(tmhd)_{12}(H_2O)$, [14], and $Ba_2(thd)_4)_3(H_2O)$ [15]. In the following, it is not differentiated between these different compounds. They are all called "$Ba(thd)_2(H_2O)_2$", and the product of their sublimation "$Ba(thd)_2$". All of these compounds are similar to each other, but have different vapor pressures. Another problem of the Ba chelate compounds (to a lesser extent, this is also true for the $Sr(thd)_2$) is the tendency to hydrolize and to oligomerize. In order to diminish the oligomerization tendency of the Ba (and also Sr) compounds the coordination sphere of the metal can be saturated by neutral ligands such as tetraglyme or phenantroline [16]. The evaporation of most thd compounds is very stable with the time. Therefore, thd compounds are very good candidates for the CVD processes of per-

ovskites, but also for other materials such as Y-stabilized heat barrier coatings [17]. An exception are the Ba and Sr compounds because of the reasons mentioned.

PRINCIPLES OF EVAPORATION SYSTEMS

The CVD process consists of different steps: the preparation unit of the reaction gas, the CVD reactor, and the exhaust unit. The first CVD equipments for the production of superconductors had—as is usual in the CVD technique—three different thermal evaporators for the three different elements Y, Ba, and Cu [18]. This method has the disadvantage that

- the evaporation temperature must be very exactly controlled for three sources,
- the evaporation rate (not only the vapor pressure!) must be very exactly known, which is very difficult to meet for the Ba precursors, and which depends on impurities and on the grain size in the case of sublimation, and
- the evaporation (especially sublimation) rate is not always constant with the time due to a) it depends on the decomposition and/or oligomerization phenomena and b) the surface of subliming substance diminishes during the sublimation.

These problems were the reason to develop single source systems. Hiskes *et al.* [19] used a mixture of powder and moved this powder through a tube to the end where the powder was flash evaporated. Samoylenko [20] used vibration equipment in order to transport the powder mixture into a heated zone where again the powder is flash evaporated. A similar equipment, but with a different powder feeder, was used in [17].

Another class of evaporators are the single sources which use a solution of all necessary precursors in one solvent. The liquid diglyme $C_6H_{14}O_3$ is mostly used as solvent for the β diketonates. They can be solved in diglyme without exchange reactions between the precursors, and barium precursor could even be stabilized with diglyme [13]. This compound has a high vapor pressure that is useful for the nebulization process described below. In the opposite case, a change of concentration would occur during the nebulization by evaporation of the solvent. The typical mole fraction of each thd compound in diglyme is approximately 0.02. Two different evaporation systems are applied:

- Droplets of the precursor-containing solution are generated by ultrasonic nebulization or by use of injection valves. Then the droplets are conducted through a heated zone where the droplets evaporate. Different classes of deposition processes can be carried out with these droplets as is shown in Fig. 1 [9]. In the first mode, the droplets impinge onto the heated surface and form the

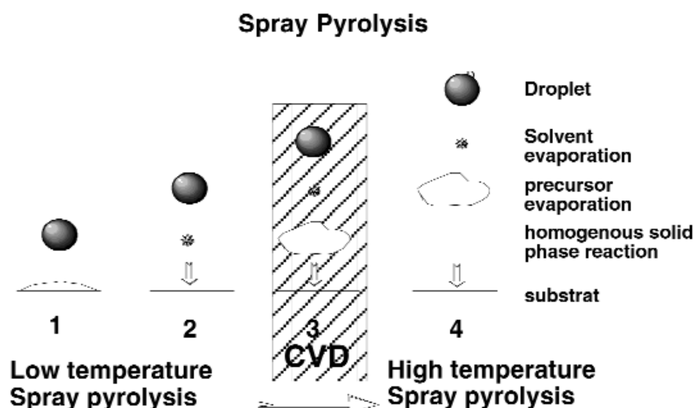


Fig. 1 Ranges of droplet-induced deposition processes.

layer. In the second mode, only the solution evaporates. In the third mode, the "CVD mode", the total droplet evaporates, and a reaction gas containing only molecules (and no particles) is formed, reactions occur only at the surface. In the fourth mode, the droplets evaporate also completely, but also homogeneous reactions occur in the gas phase. The advantage of this method is the very high flexibility of the process. The transport of the precursor until very near to the deposition surface (mode 1 in Fig. 1) in the droplet can also be useful for conditions where the precursor must be protected against the gas which occurs (e.g., in the flame CVD [21]) where the precursor would burn in the flame.

- A tape is wetted with the solution and dried either separately from the CVD process or in a procedure that is integrated with the CVD setup. The tape can also be wetted by the sequence of separated spots with different precursor combinations, and then multilayer coatings can be produced by pulse evaporation of the precursor microportions [22]. The band can be transported either continuous or discontinuous. An example for the last method is the tape reactor shown schematically in Fig. 2. In this evaporator a fiber band loop is continuously fed by the precursor solution. The condensate on the tape is then transported through a zone which is heated to the evaporation temperature T_e of the solvent, in the case of diglyme $T_e = 60$ °C, and then into a hot zone where the precursor is evaporated. The gas containing the solvent molecules are separated, and the gas containing the precursor molecules is conducted into the reactor.

Which of these methods have to be used depends on the deposition kinetics of the process. The disadvantage of the first class can be the large quantity of solvent in the gas phase. This can decrease the oxidation potential in the gas and support carbonate formation. In the following, this problem is discussed for the example of YBaCuO deposition.

THERMODYNAMIC CONSIDERATIONS

At HTCVD it can often be assumed that at the surface thermodynamic equilibrium is reached. For this case, the influence of the solvent on the CVD process is discussed for the example of the superconductor deposition.

The reaction gas for YBaCuO deposition contains O_2, Ar, or N_2 the solvent molecules, and the $M(thd)_x$ molecules. The main inlet parameters are total pressure p_{tot}, temperature T, and mole fractions x( ) of the following compounds in argon: $x(O_2)$, $x(Y(thd)_3)$, $x(Ba(thd)_2)$, $x(Cu(thd)_2)$, and x(diglyme).

The main limitation of YBaCuO crystallization in aerosol process arises from solvent burning [23]. There is a competition between crystallization of the YBaCuO and formation of $BaCO_3$:

$$2\ YBa_2Cu_3O_{7-y} + 3CO_2 = Y_2BaCuO_5 + 3BaCO_3 + 5CuO + (1-y)/2\ O_2$$

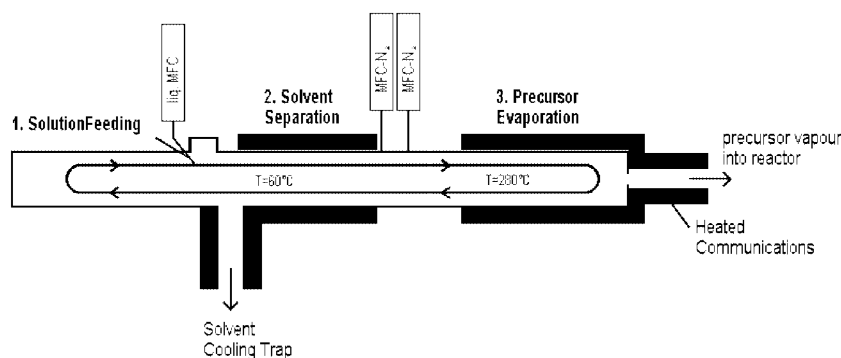
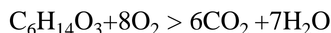


Fig. 2 Band evaporator.

Respectively, the partial pressure of CO_2 in the gas phase is the main limiting factor for the crystallization of YBaCuO. CO_2 in the CVD reactor originates from the oxidation of diglyme because always x(precursor) << x(diglyme). The total oxidation of diglyme is described by the equation



$$C_6H_{14}O_3 + 8O_2 > 6CO_2 + 7H_2O$$

Thermodynamic calculations based on the full oxidation scheme were reported [24]. This implies the limitation

$$x(O_2) > 8\ x(\text{diglyme})$$

With the molar fraction of the thd compounds in diglyme ~0.02, this means that the maximum precursor concentration is app. 0.002 what would limit the deposition rate. But the assumption of the complete oxidation is rather questionable.

The incomplete oxidation of diglyme was found experimentally by mass-spectrometric probe directly in the HTCVD reactors [25]. The advancement of the oxidation and resulting concentration of CO_2 was found to be highly dependent on the vapor residence time at the high temperature in the reactor. Application of the cold-wall CVD reactors with inductive heating of the substrate practically removes the problem of CO_2. Not only YBaCuO, but also essentially less-stable BaO can be obtained without admixture of $BaCO_3$.

On the other hand, in the hot-wall reactor, depending on the reactor design and process conditions, the diglyme vapor residence in the hot zone can be high enough to increase the CO_2 concentration, which makes YBaCuO unstable. Figure 3 shows the assignment of the partial pressures of O_2 and CO_2 measured in a CVD stagnation flow reactor to the Y–Ba–Cu–O–CO_2 phase diagram. The deposition experiments were carried out in cold- and hot-wall reactors (cold wall: the cross in Fig. 3). The YbaCuO phase area is limited by the bold lines and on the right side by the lines with the CO_2 partial pressure as parameter (measured in atm). The CO_2 partial pressure expected from the diglyme flow would be much higher in the thermodynamic equilibrium than in the experimental equipments.

The possibility of substitution of copper by CO_3^{-2} in the high T_c cuprates during MOCVD was demonstrated recently [26]. The substitution can deteriorate the superconducting properties at the lower P_{CO2} then necessary for the decomposition of YBaCuO.

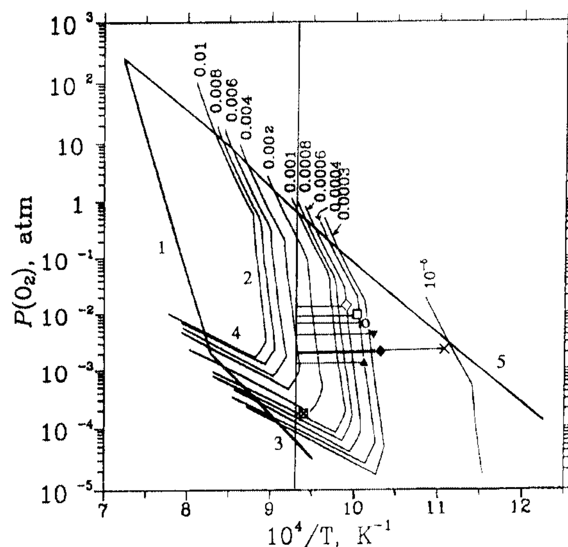


Fig. 3 Deposition temperature 800 °C, total pressure 10 mbar, oxygen partial pressure 2.7 –15 mbar (detailed conditions [25]).

According to the thermodynamic calculations, some highly stable perovskites like $BaTiO_3$ would form even at the high partial pressure CO_2 pressure under MOCVD conditions, but an experimental test for this is lacking.

Size scaling of the HTCVD reactors for the industrial applications would increase the vapor residence time in the hot zone, resulting in the deeper oxidation of solvent and production of higher CO_2 concentration. So, for such purposes a separation of the solvent from the reaction gas can be recommended. For industrial applications this is an important condition, therefore the band evaporator is preferable.

Another thermodynamic respect comes from the account of surface energy contribution, which should not be neglected for the thin films. Recently [27,28], it was shown that surface and interface energies can change the equilibrium phases in thin films. The formation of phases is preferred, which can form coherent interface with the substrate and/or YBaCuO matrix. In particular, in the case of the $YBa_2Cu_3O_{7-\delta}$ deposition, Y_2O_3 forms as secondary phase instead of Y_2BaCuO_5 which is thermodynamically stable and coexists with $YBa_2Cu_3O_{7-\delta}$ in the bulk state. Similarly in Ba-enriched YBaCuO films the formation of $BaCu_3O_4$ was observed, which does not appear on the equilibrium phase diagram of the bulk state.

KINETICS OF THE CVD FROM THD COMPOUNDS IN A MICROBALANCE

The temperature behavior of the deposition rate is shown for a stagnation geometry, whereby the band evaporator was used as a gasification system. The curves show the typical behavior of a CVD process: At high temperature a small temperature dependence (diffusion-controlled process) and at low temperature an almost linear dependence, which is a hint of an activated process. The deposition rate in the diffusion-controlled range can be estimated in the stagnation point by the formula [29].

$$j = \alpha D \frac{x(prec)n}{d} \mathrm{Re}^{1/2} Sc^{1/3}$$

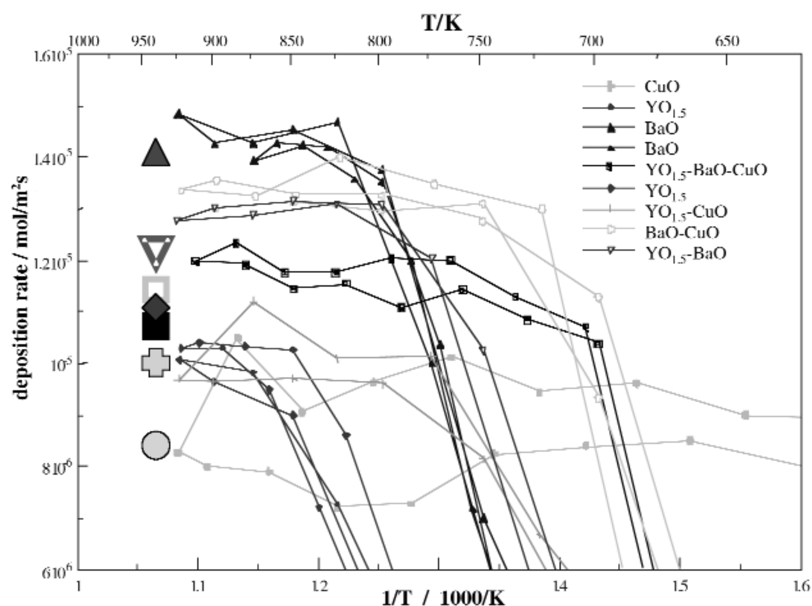


Fig. 4 Deposition experiments, total pressure 1000 hPa, gas flow 15 l/h, large points: calculated.

whereby α is an empirical constant in the range of $\alpha = 1$ (we take $\alpha = 1!$), D is the diffusion coefficient, estimated with the methods given in [30], d is the nozzle diameter, Sc the Schmidt number $Sc = \eta/\rho D$ (η = dynamic viscosity, ρ = mass density) and Re the Reynolds number $Re = \rho v d/\eta$ (v = entrance gas velocity). According to this formula the deposition process is proportional to the mol fraction of the precursor and proportional to the root of the gas velocity. More exactly and in addition on every point—not only at the stagnation point—the deposition rates were calculated with the code Fluent [31]. The results calculated and plotted in Fig. 4 [32] show quite a good accordance with the measured values. This shows that in this geometry are very few side reactions which would decrease the deposition. The thermodiffusion was included in these calculations, but the effect was not large (<20%).

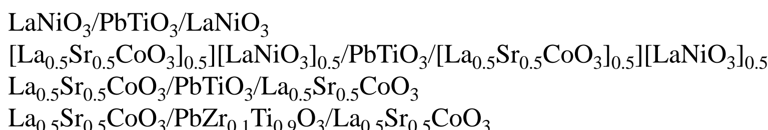
SPECIAL REACTORS AND APPLICATIONS

Experiments in the stagnation flow reactor

As mentioned, with the help of band flash evaporator it is possible to deposit multilayer structures supplying different precursors from the band. For instance, the following epitaxial heterostructures

(001)$CaRuO_3$/(001)PrO_x/(001)YSZ
(001)$CaRuO_3$/(001)CeO_2/(1–102)Al_2O_3

consisting of buffer layers and $CaRuO_3$ perovskite electrodes were obtained in a continuous deposition run with subsequent deposition on top ferroelectric $PbTiO_3$ layers by this technique [33]. Using a flash evaporation system with vibrating feeder, fully epitaxial perovskite thin film capacitors consisting of top and bottom electrodes with intermediate ferroelectric layer were obtained on MgO substrate [34]:


$LaNiO_3/PbTiO_3/LaNiO_3$
$[La_{0.5}Sr_{0.5}CoO_3]_{0.5}][LaNiO_3]_{0.5}/PbTiO_3/[La_{0.5}Sr_{0.5}CoO_3]_{0.5}][LaNiO_3]_{0.5}$
$La_{0.5}Sr_{0.5}CoO_3/PbTiO_3/La_{0.5}Sr_{0.5}CoO_3$
$La_{0.5}Sr_{0.5}CoO_3/PbZr_{0.1}Ti_{0.9}O_3/La_{0.5}Sr_{0.5}CoO_3$

According to XRD bottom and top layers were (001) oriented and the ferroelectric layer consisted of a- and c- oriented domains as it can be seen from the HREM image of the cross-sectioned heterostructure $La_{0.5}Sr_{0.5}CoO_3/PbTiO_3/$ $La_{0.5}Sr_{0}.5CoO_3$. At some parts of these structures cracks crossing all three layers were revealed by HREEM. Possible reason of the crack formation are mechanical strains appearing owing to the ferroelectric phase transition in the intermediate layer. In spite of extremely high surface smoothness of bottom electrode layers (doped La cobaltate, La nickelate or their solid solutions) the resulting heterostructure has much rougher surface. This can be a result of kinetic hinderance in CVD of ferroelectric layer.

The structure can probably be improved by simultaneous irradiation of photons. In the case of $PbTiO_3$ deposition the crystallinity and the nucleation behavior of the grown layer can be changed [35–38].

Deposition of superconductors on tapes

For industrial applications tapes have to be coated. The construction of the equipment had to take into account the following boundary conditions: It must be mainly a cold-wall reactor, which means the reaction gas must not a have contact to hot surfaces before the deposition and there must be a small residence time in the hot zone in order to diminish the number of side reactions. On the other side, the substrate changes the emission coefficient during the deposition. Therefore, it is difficult to stabilize the temperature by radiation heating in a cold-wall reactor. The compromise between these both demands is a hot furnace. The main element is the hot reactor tube with a length of 5 cm and an internal diameter of 4 cm, which is heated by resistance heating. The reactor is closed on all sides to establish an equilibrium temperature. Only small holes and slits are in the cylinder for the gas flow and the tape trans-

port. Through the hole at the top and at the basis the reaction gas is conducted to the substrate tape (e.g., ZrO_2) which is transported through slits at the side of the reactor. On the tapes, also, single samples can be deposited. The gas flow through the reactor is thus adjusted, then the contact of the reaction gas with the walls before the deposition process is minimized. These results were supported by simulations with the code FLUENT. Small tape velocities of 3–20 cm/h are reached until now in order to deposit on the tapes. For increasing the deposition velocities different reactors in series have to be used [39].

PERSPECTIVES

The CVD process from chelates has a number of other applications. One example should be mentioned here. Thermal protection systems can contribute significantly in the reduction of NOx emission in the combustion systems of aircraft engines and stationary gas turbines. There are in development fiber-reinforced composites and heat barrier coatings. In both ceramic layers are demanded: The fibers have to be coated with ZrO_2 [17], and the turbine turbine blades have to be coated with Y-stabilized ZrO_2. This is done today with electron beam evaporation or plasma spraying. But it might be that in the future HTCVD coating will have to be used. The CVD process is principally simpler at good quality and because it is a no line of sight process it is easier to coat complicated forms like turbine blades [40]. As precursors, $Y(thd)_3$ and $Zr(thd)_4$ can be used

REFERENCES

1. G. Wahl, M. Pulver, W. Decker, L. Klippe. *Surf. Coat. Technol.* **100–101**, 132–141 (1998).
2. C. Metz and G. Wahl *et al.,* Lecture presented at the 10th International Conference of High Temperature materials Chemistry (HTMC-X), Jülich, Germany, 10–14 April 2000.
3. R. Stolle and G. Wahl. *Chem. Vap. Dep.* **6**, 83 (2000).
4. F. Weiss, J. P. Senateur, J. Lindner, V. Galindo, C. Dubourdieu, A. Abrutis. *J. Phys. IV* France 9 Pr8, 283 (1999).
5. O. Stadel, J. Schmidt, G. Wahl, C. Jimenez, F. Weiss, M. Krellmann, D. Selbmann, N.V. Markov, S. V. Samoylenkov, O. Yu. Gorbenko, A. R. Kaul. Proc. M^2S-HTSC VI, Houston, *Physica C* **341–348**, 2477–2478 (2000).
6. A. Yamane, H. Kurosawa, T. Hirai. *Chem. Lett.* 939 (1988).
7. K. H. Dahmen, T. Gerfin. *Prog. Cryst. Growth* **109**, 401 (1991).
8. M. Leskela, H. Molsa, L. Niinisto. *Supercond. Sci. Technol.* **8**, 67 (1995).
9. G. Wahl, F. Weiss, O. Stadel. "Deposition Technique: Chemical Deposition". In *Handbook of Superconducting Materials*, D. Cardwell and D. Ginley (Eds.), Inst. of Physics, Bristol (2000).
10. M. L. Hitchman, K. F. Jensen. *Chemical Vapor Deposition*, Academic Press, London (1993).
11. M. Pulver. Thesis, TU Braunschweig (1999).
12. S. B. Turnipseed, R. M. Barkley, R. E. Sievers. *Inorg. Chem.* **30**, 1164 (1991).
13. A. A. Drozdov, S. Troyanov, A. Pisrevski, Y. Struchkov. *J. Phys. IV* Coll C5, suppl-*J. Phys. II* C **5**, 503 (1995).
14. A. A. Drozdov, S. Troyanov, A. Pisrevski. *Polyhedral* **13,** 2459 (1994).
15. O. Gorbenko. Inst. of Chem. Lomonossov Univ. Moscow priv. comm., March 2000.
16. N. Kuzmina, V. Ivanov, S. Troyanov, I. Malkerova A. Alikhanyan. *J. Chem. Vap.* **1**, 72–84 (1995).
17. K. Nubian, B. Saruhan, B. Kanka, M. Schmücker, H. Schneider, G. Wahl. *J. Europ. Cer. Soc.* **20**, 537 (2000).
18. F. Schmaderer, R. Huber, H. Oetzmann, G. Wahl. *J. Phys. IV* Coll. C2 suppl. *J. Phys. II* **1**, 539 (1991).
19. R. Hiskes, S. A. DiCarolis, J. L. Young, S. s. Laderman, R. D. Jacowitz, R. C. Taber. *Appl. Phys. Lett.* **59**, 606 (1991).

20. S. V. Samoylenko, O. Y. Gorbenko, I. E. Graboy, A. R. Kaul, Y. D. Tretyakov. *J. Mater. Chem.* **6**(4), 623 (1996).
21. Abschlußbericht des Forschungs- und Entwicklungsvorhabens 13N6518 1998, Voruntersuchungen zur Abscheidung bei hohem Druck, Bundesministerium für Bildung und Forschung, Bonn.
22. A. R. Kaul and B. V. Seleznov. *J. Phys. IV* Coll c3 **3**, 375, 225 (1993).
23. W. Decker, Yu. Erokhin, O. Gorbenko, I. Graboy, A. Kaul, A. Nurnberg, M. Pulver, R. Stolle, G. Wahl. *J. Alloys & Comp.* **195**, 291 (1993).
24. F. Weiss, A. Pisch, C. Bernard, U. Schmitz. *J. Phys.* Coll. C5 suppl. *J. Phys. II* **5** C5 151 (1995).
25. Y. Erokhin, O. Gorbenko, I. Graboy, A. Kaul, S. Pozigun, W. Decker, R. Stolle, G. Wahl. *Proc. VI Trilateral Seminar on High T_c Superconductivity*, Dubna, 95 (1994).
26. K. Chang, B. Wessels, W. Qian, V. P. Dravid, J. L. Schindler, C. R. Kannewurf, D. B. Studebaker, T. J. Marks, R. Feenstra. *Physica C* **303**, 11 (1998).
27. S. V. Samoylenko, O. Yu. Gorbenko, I. E. Graboy, A. R. Kaul, O. Stadel, G. Wahl, H. W. Zandbergen. *J. Phys. IV* 9 Pr 621 (1999).
28. A. Kaul. Lecture presented at the 10th International Conference of High Temperature Materials Chemistry (HTMC-X), Jülich, Germany, 10–14 April 2000.
29. D. T. Chin and C. H. Tsang. *JECS* **125**, 1461 (1978).
30. R. C. Reid, J. M. Prausnitz, B. E. Poling. *The Properties of Gases and Liquids*, Wiley, New York (1987).
31. *Users Guide for Fluent Release 4.4*, Fluent Inc, Lebanon NH, USA (1966).
32. L.Klippe. Thesis, TU Braunschweig (1998).
33. A. A. Molodyk, M. A. Novozhilov, I. E. Graboy, O. Yu. Gorbenko, I. E. Korsakov, A. R. Kaul. *Chemical Vapor Deposition, Proceedings of the XIV Int. Conf. and EUROCVD-11*, M. A. Allendorf and C. Bernard (Eds.), Paris, p. 1152 (1997).
34. M. A. Novozhilov, A. R. Kaul, O. Yu. Gorbenko, I. E. Graboy, G. Wahl, U. Krause. *J. Phys. IV France* 9, Pr8-629 (1999).
35. M. Shimizu, T. Katayama, M. Fujimoto, T. Shiosaki. *Proc. Intern. Conf. on Thin Film Physics and Application*, Shanghai (1991).
36. T. Katayama, M. Fujimoto, M. Shimizu, T. Shiosaki. *J. Cryst. Growth* **115**, 3005 (1991).
37. A. Ando, T. Katayama, M. Shimizu, T. Shiosaki. *Jpn. J. Appl. Phys.* **31**, 3001 (1992).
38. U. Krause. IOPW Report, Institut für Oberflächentechnik, Braunschweig, Germany (1999).
39. O. Stadel, priv. communication, Inst. für Oberflächentechnik, Braunschweig, Germany, March 2000.
40. M. Pulver, W. Nemetz, G. Wahl. *Surf. Coat. Technol.* **125**, 400 (2000).