Preparation of thin epitaxial multilayer $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}(\text{Ag})$ films by aerosol deposition

F HANIC, M JERSEL[†], S CHROMIK[†], G PLESCH and
V ŠTRBIK[†]

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia

[†]Electrotechnical Institute, Slovak Academy of Sciences, 842 39 Bratislava, Czechoslovakia

Abstract. Thin-textured $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films were prepared by a new CVD process consisting of aerosol deposition and low temperature annealing, both operations not exceeding 600°C. MgO and SrTiO_3 single crystals were used as substrates. The stoichiometry of the prepared films was not ideal 1–2–3, having the atomic quotient of copper always lower than 3. For an unoptimized preparation process, the onset temperatures were around 80 K and the zero resistance T_c values around 70 K. Properties of samples obtained by low-temperature annealing are compared with those obtained by high temperature annealing. “Cleaning” effect of vacuum-annealing upon removing the nitrate and hydroxide groups from the prepared films is supposed.

Keywords. Superconductivity; epitaxy; aerosol deposition; superconducting films.

1. Introduction

High- T_c superconductors with a high critical current density $J_c = 10^6$ to 10^7 A/cm² at 77 K/0 T (in magnetic field 0 T) have been produced only as thin epitaxial films on oxide substrates SrTiO_3 or MgO (Chaudhari *et al* 1987; Enomoto *et al* 1987; Itozaki *et al* 1988; Kwo *et al* 1988; Hwang *et al* 1989). The use of other substrate materials has not resulted in such high current densities because of chemical reactions between the superconducting film and substrate (provided that the heat treatment was performed at 650 to 900°C) as well as due to the lattice strain caused by the mismatch of lattice parameters and different thermal expansion coefficients. For instance, both SrTiO_3 and $\text{YBa}_2\text{Cu}_3\text{O}_y$ are perovskite-type oxides with nearly equal lattice parameters in two directions. Thus, there is a minimum of deformation interaction between the substrate and the thin film and a strong substrate effect exists upon the epitaxial growth of the deposited film. There have been attempts to improve the superconducting properties or to facilitate fabrication of superconducting films on inexpensive and easily available substrates by using diffusion barriers or buffer layers as ZrO_2 or $\text{ZrO}_2\text{-SiO}_2$ separating the superconductor from reactive substrates like Si. However, in such a case the epitaxial effect of the substrate upon the deposited film is suppressed and the J_c value is rather low, about 5×10^3 A/cm² at 4.2 K/0 T (Mogro-Campero *et al* 1988). The critical current density J_c in sintered polycrystalline bulk samples is also low, being about 10^2 to 10^3 A/cm² at 77 K/0 T but it can be improved to about 10^4 A/cm² at 77 K/0 T with melt texturing or directional solidification (Jin *et al* 1988).

Various techniques for preparation of high- T_c superconducting materials are now available (Jerger 1989) and among them the chemical thermal decomposition methods are of primary importance. As an example the following methods may be mentioned: the sol-gel method, aerosol deposition or spray pyrolysis, chemical vapour deposition, plasma spraying, pyrolysis of metallic salts, melt-textured growth, liquid phase

epitaxial growth, etc. In principle, some of these methods are inexpensive and are also suitable for continuous production of superconducting tapes or fibres. In this paper we deal with low temperature aerosol deposition followed by low-temperature annealing. This method allows a broad application of various substrates as well as continuous production of highly oriented multilayer thin films with a controlled thickness.

Thin and thick films of the Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O systems were earlier prepared by aerosol deposition or spray pyrolysis by Kudas *et al* (1989a,b). They used nitrate solutions of metallic components to prepare $\text{YBa}_2\text{Cu}_3\text{O}_y$ films about 1 mm thick on the inner surface of the copper tube annealed at 880°C for 1–2 h in oxygen. A very sharp superconducting transition was detected at 92 K with a rather low J_c value being about 10^1 to 10^2 A/cm² at 77 K/0 T. Also powders of Bi–Sr–Ca–Cu–O and Tl–Ca–Ba–Cu–O systems were already prepared by this method.

Thin films of $\text{YBa}_2\text{Cu}_3\text{O}_y$, $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ were prepared by spray pyrolysis by Henry *et al* (1989). They used spray pyrolysis of aqueous nitrate solutions, MgO single crystal as a substrate and oxygen as a propellant gas. During spraying, the substrate temperature was kept at 300–875°C, annealing was performed at 960°C in the case of $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ and, 850°C in the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. Film thicknesses were 3–7 µm, and zero resistance T_c values, $T_c = 77$ K for Y-system, 74–81 K for Y(Ag)-system and $T_c = 65$ K for Bi-system.

In what follows a chemical deposition process is described, which allows preparation of thin $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films at temperatures not exceeding 600°C. Our procedure consists of two steps. First, thin films are sprayed over MgO or SrTiO_3 substrates at temperatures below 600°C, annealing then follows in a good vacuum degraded by partial pressure of oxygen, at temperatures around 600°C. During this second step, the remnants of nitrate and hydroxide groups are removed from the films. Some films were first annealed at 900°C. Their mutual properties are compared and the preliminary results are described.

2. Experimental

As mentioned above, the process of sample preparation was divided into two steps: first, deposition of aerosol was performed by spraying onto hot substrate and final annealing then followed.

The nitrate solutions used for growing $\text{YBa}_2\text{Cu}_3\text{O}_y$ films were prepared by dissolving stoichiometric quantities of $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water and, by adjusting the solution concentration to 0.05 mol/l and pH to 2. The solution for growth of composites $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ was prepared by admixing AgNO_3 to 0.05 mol/l nitrate solution such that the solution contained 10 wt.% Ag regarding the mass of $\text{YBa}_2\text{Cu}_3\text{O}_y$ in nitrate solution (i.e. 5.25 g AgNO_3 /l).

Formation of the chemically homogeneous particles of nitrate solution occurred in an aerosol generator using oxygen as a propellant gas. The stable aerosol stream of fine droplets was then led into the particle separator from which a very fine submicron particle vapour stream was sprayed over MgO single crystal substrate. Aerosol was deposited at substrate temperatures 120–180°C for 20 min during one-deposition cycle, followed by heating up to 500–580°C in air for 10 min with the aim of dehydration and pyrolysis of nitrates. This heating also led to epitaxial growth of oriented tetragonal form of $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$. After cooling down to the substrate

temperature 120–180°C, the whole cycle was repeated with the deposition of another $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ -oriented layer. Films were also deposited on SrTiO_3 single crystal substrates to ascertain the substrate-texturing influence. Altogether 5 to 11 such cycles were performed to obtain a complete multilayer film consisting of various combinations of Y–Ba–Cu–O sublayers with or without Ag-doping.

The crucial point of preparation of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films was the oxidation process (final annealing) performed either at high temperatures (900°C) at atmospheric pressure, or at low temperatures (600°C) in vacuum degraded by oxygen, or under conditions of a combination of both. Of course, for us low-temperature final annealing was the most important.

The low temperature annealing consisted also of two steps (Chromik *et al* 1989). First, the samples were heated to about 600°C in a vacuum chamber evacuated by oil diffusion pump initially to 10^{-4} Pa, with vacuum then degraded by oxygen to 10^{-2} Pa, without changing the substrate temperature. Oxygen pressure was then increased from 10^{-2} to 5 Pa without changing the initial substrate temperature. During this step a transition from tetragonal to orthorhombic form took place due to the shift of phase transition temperatures (Schuller *et al* 1987). The intercalation of oxygen into the Cu–O planes also occurred. As a next step, the substrate temperature was decreased to 400°C followed by rise of oxygen pressure to atmospheric pressure. Finally, the samples were slowly cooled down to room temperature at the atmospheric pressure of oxygen.

In the case of high temperature final annealing, samples were annealed at 900°C for 20 min followed by intercalation of oxygen at 500°C for 60 min and slowly cooled down, all at atmospheric pressure.

All the prepared samples were then characterized by measuring the $R(T)$ dependence, using the dc four-point resistive method. The composition of superconducting films was examined by energy-dispersive X-ray analysis (EDAX). X-ray diffraction patterns were taken on a Philips powder diffractometer using CuK_α radiation.

3. Results, discussion and conclusions

We now describe some preliminary results. The optimization of the whole preparation process is now on the way.

After the first preparation step (deposition of aerosol onto substrate) all the films showed semiconducting or metallic conductivity, even though the $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ phase was already a well-developed compound in the form of textured films after 5 to 7 deposition cycles.

The $R(T)$ dependence for two $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films, both prepared on MgO substrates, is presented in figure 1. The dashed line 1 applies for samples with high temperature final annealing (as mentioned earlier, the annealing process was not optimized). The onset temperature here is slightly greater than 80 K, but the transition ΔT_c is broad with the zero resistance T_c value around 30 K. When the same sample was also low-temperature annealed, the T_c value increased to about 70 K (line 2). For comparison, the $R(T)$ dependence is plotted for another sample, annealed at low temperatures only (line 3). The properties are similar to those represented by line 2. The number of deposition cycles for the described samples was 5 and 7 and the total film thickness was about 1 μm .

When the number of deposition cycles was increased to 11 in the case of SrTiO_3

Figure 1. $R(T)$ dependence for two $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films prepared on MgO substrate. 1. sample S-10, high temperature (900°C) annealed, 2. sample S-10, high (900°C) and low temperature (600°C) annealed, 3. sample S-14, annealed at low temperatures only (600°C).

Figure 2. $R(T)$ dependence for $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ film prepared on SrTiO_3 substrate (S-13). 1. high temperature (900°C) anneal; 2. high (900°C) and low temperature (600°C) anneal.

single-crystal substrate, the film thickness also increased to about 2 to $3\ \mu\text{m}$ and the multilayer film was neither oriented nor superconducting. Figure 2 shows the $R(T)$ dependence of such a film after high temperature (line 1), and low temperature additional annealing (line 2). The behaviour of the deposited film was semiconducting after the first annealing. After low temperature annealing the $R(T)$ dependence was similar to those presented in figure 1, with zero resistance T_c value being about 70 K.

EDAX analyses show homogeneous composition of the prepared films around the whole sample surfaces; however, the stoichiometry was not exactly ideal as 1–2–3. The atomic quotient of copper was always slightly lower than 3.

X-ray diffraction patterns for samples shown in figures 1 and 2 may be seen in figure 3a, b. Figure 3a represents well-oriented and textured films prepared on single crystal MgO substrate with 5 (lines 1. and 2. of figure 1) and 7 (line 3. of figure 1) deposition cycles. Figure 3b applies to diffraction pattern of sample presented in figure 2. In this case single crystal SrTiO_3 substrate was used and the $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$

Figure 3. X-ray diffraction patterns for: **a.** oriented and textured films of samples S-10 and S-14 of figure 1 and **b.** unoriented film of samples S-13 of figure 2.

film with thickness 2 to 3 μm consisted of 11 layers. This film was unoriented after the deposition process and remained so even after final annealing.

For evaluation of c parameter of a fully textured film containing only 001 lines, the following formula was used:

$$c = (\lambda/2 \sin \Delta\theta)(l_1 \cos \theta_{001_2} - l_2 \cos \theta_{001_1}), \quad (1)$$

Figure 4. Evaluation of the unit cell parameter from the indexed X-ray powder diffraction diagram (figure 3a) using (1). The c value is extrapolated according to the known dependence c upon y .

in which $\Delta\theta$ is the difference in diffraction angles of the diffraction lines 001_1 and 001_2 .

Introduction of $\Delta\theta$ into evaluation of the lattice parameter c by (1) instead of using the usual formula $c = \lambda/2 \sin \theta_{001}$ minimizes the so-called "zero point error". For the system of diffractions: $\theta_{002} = 7.62^\circ$, $\theta_{003} = 11.45^\circ$, $\theta_{004} = 15.34^\circ$, $\theta_{005} = 19.31^\circ$, $\theta_{006} = 23.37^\circ$, $\theta_{007} = 27.54^\circ$, the least square refinement of the linear dependence c vs $\sin \Delta\theta$ gave the value 11.681 (16) Å extrapolated to $\sin \Delta\theta = 1$, with a correlation coefficient $R = 0.999$. The results of the c parameter evaluation may be seen in figure 4. The value of 11.681 (16) Å indicates the formula $\text{YBa}_2\text{Cu}_3\text{O}_7$, according to the known dependence of y vs c (Muradyan *et al* 1989).

In conclusion we may say that we have succeeded in preparing thin well-oriented and textured superconducting $\text{YBa}_2\text{Cu}_3\text{O}_y(\text{Ag})$ films. These films were prepared by a combination of aerosol deposition and low-temperature annealing process, which seems to be a necessary condition for obtaining "clean" superconducting films, free of used nitrate and hydroxide groups. The results are promising and therefore, as a next step, the optimization of our preparation process will follow. Two important results may be stressed as far as this preparation procedure is concerned: the use of a simple and inexpensive spray deposition method suitable also for continuous production and the use of temperatures not exceeding 600°C .

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