

Low-pressure single aerosol source MOCVD of YBCO thin films

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Abstract

YBCO thin films are obtained by low-pressure aerosol version of MOCVD technique. The effects of different process factors are studied. The conclusion is made that the main disadvantage of the process is the high partial pressure of carbon dioxide in the deposition zone. The ways to improve the situation are considered.

1. Introduction

Metalorganic chemical vapor deposition (MOCVD) is one of the promising techniques for HTSC thin films *in situ* fabrication. The possibility to obtain high quality films of YBCO and BSCCO systems on large surfaces was demonstrated by many groups. In spite of this the reproducible preparation of multicomponent films with stoichiometric ratio of cations is still the challenge for the technique. This is mainly due to relatively poor reproducibility of metalorganic compounds (MOC) volatility and its strong dependence on evaporation temperature and carrier-gas flow. The necessity of very precise temperature and mass-flow control of each component vapor source makes the device overcomplicated. Two alternative single source approaches have been developed to solve the problem. The first is flash evaporation of MOC powder mixture [1]. Another technique consists in the deposition from vapor phase obtained by the evaporation of sprayed MOC solution [2]. In the latter work the deposition was realized at normal (atmospheric) pressure and attempts to reproduce the results demonstrated that the process was difficult to control. We believe the low pressure version of aerosol CVD to be more controllable due to increased MOC volatility. Low oxygen pressure at the deposition stage also promotes the epitaxial growth of YBCO films [3]. In this paper we make an attempt to develop the low pressure aerosol version of MOCVD of YBCO films and to study the role of different process factors.

2. Experimental

Chelate complexes with 2,2,6,6-tetramethyl-3,5-heptanedione Y(thd)₃, Ba(thd)₂ and Cu(thd)₂ were used as volatile precursors. A number of organic solvents (n-hexane, n-decane, n-dodecane, n-butanol, diglyme and N,N-dimethylformamide) were tried. It was demonstrated that diglyme and n-decane are most suitable as they possess low viscosities, sufficiently high boiling points and ability to dissolve Me(thd)_n complexes. The concentration range was 0.001-0.01 M. The aerosol of MOC solution was generated by evacuated ultrasonic nebulizer giving droplets of narrow size distribution and medium diameter of 3-5 μm. The flow of Ar (3-15 l/h) going through nebulizer carried the aerosol via the heated transport tube into the vertical reactor. After the aerosol was transformed into the vapor phase it was mixed with the flow of oxygen (30-40 l/h) and directed onto the heated substrate. Two experimental devices which differ mainly in aerosol flow heating mode were used. The first (D1) includes a separate heater on the transport tube to evaporate the solvent and the precursors. In this case evaporation temperature was constant (270°C) and independent of the substrate temperature. The transport tube of another device (D2) was heated by the radiation of the substrate heater. In this case the solvent and precursors evaporation occurred in the temperature gradient rising toward the substrate. After the deposition time (15-40 min) the films were slowly cooled at P_{O₂} = 1 atm.

The films obtained were characterized by X-ray

diffraction, SEM and EDAX analyses. ESCA and Auger spectroscopy were used to control residual carbon. The magnetic susceptibility was measured by an AC susceptometer with an exciting field frequency of 100 Hz, amplitude 0.1 Oe at temperatures between 10 and 150 K. Resistance measurements were carried out using AC, 4-points technique.

3. Results and discussion

First the deposition kinetics in the terms of Me(thd)n molecules diffusion model in a stagnation flow hot wall reactor was calculated (to be published elsewhere). In order to check the conclusions derived from the calculations the modeling experiments were undertaken. They consist in deposition in isothermal stagnation cell made in a form of a small ($d=4$ mm, 20 mm long) one end open tube introduced in the substrate holder and subsequent EDAX analysis of the deposits along the stagnation cell axe. The comparison of calculated and experimental data shows that the deposition proceeds mainly in the diffusion control regime but the influence of gas phase reactions is also evident [4]. The predominant role of molecular diffusion through boundary layer is also confirmed by the fact that YBCO deposit mass is practically independent of the deposition temperature, T_d (fig.1). The reciprocal pressure dependence gives a hint that evaporation of MOC was not completed during the deposition (fig.1). The effect of total gas flow velocity ($m \sim v^{1.27}$, where m is mass of the deposit per cm^2 , v is linear flow velocity) at $P=20$ mbar and $T=850^\circ\text{C}$ exceeds the prediction for "pure" diffusion control of the deposition ($m \sim v^{0.5}$). This discrepancy is probably due to the reactions in gas phase. The effects of P and v are surely interconnected.

Thus in kinetic aspect the low pressure aerosol deposition is similar to the conventional MOCVD with individual sources of volatile precursors studied in [5,6]. Nevertheless a very important difference of these processes exists. The peculiarity of the studied process is the presence of solvent vapor in the gas flow. The exothermal effect of solvent vapor oxidation can change the thermal conditions of the deposition significantly. In a few seconds after aerosol flow was directed on the heated substrate a well pronounced increase of the temperature (ΔT) was registered by the thermocouple located on the substrate surface for all the solvents used. As it is shown on fig.2 the ΔT value increases strongly with the substrate initial temperature increase in the cases of *n*-decane and *n*-dodecane. A very important feature of solvent vapor oxidation is the dependence of ΔT on the total pressure

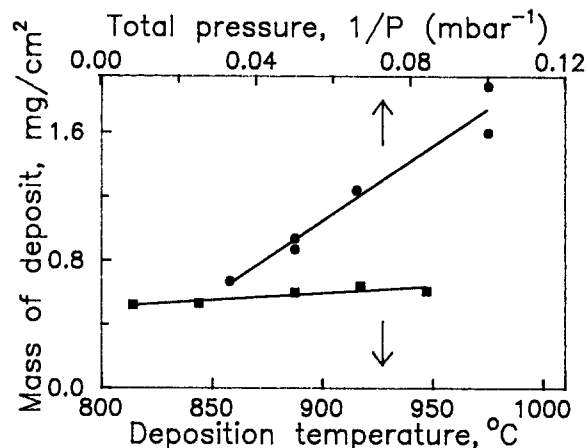


Fig.1. Pressure and temperature dependences of mass of YBCO deposits.

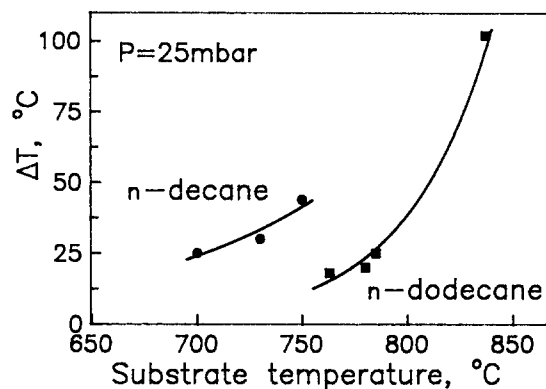


Fig.2. Deposition temperature increase vs initial substrate temperature.

in the reactor. Thus in the case of diglyme no heat evolution was observed even at substrate temperature 800°C when the total pressure was 21 mbar or less. But an increase of the pressure just to 22 mbar accelerated the oxidation process and the substrate temperature rapidly grew up to 950°C . By switching the pressure between 21 and 22 mbar rapid temperature oscillations were observed many times. It is evident that the threshold pressure at which temperature oscillations occur is dependent (as well as ΔT) on the aerosol consumption and O_2 /solvent vapor ratio. This sort of phenomena is typical of the chain reactions in gas phase. An important point is that the oxidation of a solvent does not reach equilibrium when vapor flows in the heated zone near the substrate. For example in the case of *n*-decane chromatographic and volumetric analyses of oxidation products frozen in

liquid nitrogen trap show that only 10-15% of the solvent are oxidized in spite of oxygen excess. This degree of the reaction advancement is typical of linear flow velocity of about 2 m/min (used in the device D2) and it can be obviously decreased by rising the flow velocity.

Another gas dynamic factor affecting the oxidation macrokinetics is the homogeneity of solvent and MOC vapors premixing with oxygen flow. When laminar vapor flow was not mixed enough with coaxial laminar oxygen flow the obtained films consisted of concentric areas differing in composition. We believe it to be due to the rate of oxidation across the gas inlet section being not constant. The use of mixing chamber led to predeposition effects. Judging by the uniformity of the obtained films the best mixing with rapid transport of mixed gases ($Re \approx 100$) was achieved in the narrow T-type connection.

Analytic data on starting MOC solutions and obtained films (fig.3) evidenced that the deposition process is strongly incongruent and the deviation of film composition from that of solution depends on T_d . This fact owes its origin mainly to partial MOC thermal decomposition and predeposition effects. In device D2 non completed evaporation, presumably of $Ba(thd)_2$, at low T_d was also revealed that confirms the necessity of separate aerosol evaporation stage, as in device D1.

After the MOC solution composition was corrected, the YBCO films with stoichiometry very close to 1:2:3 (according to EDAX) were obtained. X-ray diffraction shows the appearance of $YBa_2Cu_3O_x$ phase only at T_d above 750°C. Addition of N_2O to O_2 flow activates the phase formation at 750°C but the broad X-ray reflections reveal its poor crystallinity. It is worth noting that even at this temperature the film on $LaAlO_3$ (100) substrate demonstrates better crystallinity and *c*-type texture in contrast to the film on MgO (100) due to orienting effect of the substrate structure. A well pronounced "mixed" (*c*- and *a*-types) texture is a characteristic feature of the films obtained on YSZ substrates at $T_d \geq 850^\circ C$. This effect was observed both for random and (100) substrates. SEM microstructure observations manifested that melting of the films takes place at T_d about 940°C. In this case only *c*-type sharp texture ($I_{(103)(013)(110)}/I_{(006)} < 0.01$) was observed.

Magnetic susceptibility data (fig.4) reveal the progressive improvement of SC-properties with increasing T_d . The same was confirmed by resistivity measurements. The highest $T_{c(R=0)} = 79$ K was obtained at $T_d = 920^\circ C$. We believe this fact, as well as the absence of SC-transition of near stoichiometric films deposited at 750-850°C to be related with the

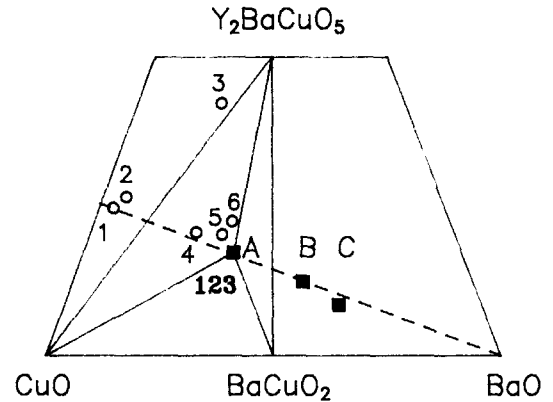


Fig.3. Correspondence between composition of starting MOC solution and that of films obtained at different T_d .

Solution A (1:2:3): 1-720°C, 2-750°C, 3-780°C
 Solution B (1:4:3): 4-720°C, 5-750°C, 6-780°C
 Solution C (1:5.10:3.26) gave the stoichiometric film at 750°C.

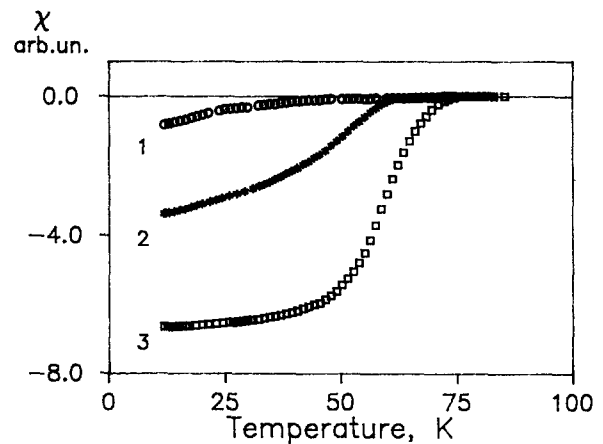


Fig.4. Magnetic susceptibility data for films obtained at $T_d = 860^\circ C$ (1), $T_d = 910^\circ C$ (2), $T_d = 920^\circ C$ (3).

presence of CO_2 which is the product of solvent oxidation during the deposition. In contrast to nonequilibrium solvent oxidation which takes place in the vapor flowing fast over the heated substrate the formation of $YBa_2Cu_3O_x$ phase at steady partial pressure of CO_2 in the deposition zone can be regarded in the context of equilibrium process. According to equilibrium phase diagram of Y-Ba-Cu-O- CO_2 system constructed in [7] the low temperature stability boundary of $YBa_2Cu_3O_x$ phase shifts strongly in the higher temperature region when the partial pressure of CO_2 increases. Using this data we estimated the minimal temperature of $YBa_2Cu_3O_x$ phase formation

(T_{\min}) at the conditions of deposition from the MOC vapor containing *n*-decane. Assuming the products of *n*-decane oxidation to be only CO_2 and H_2O and the degree of the oxidation advancement - 12% (at gas flows 15 l/h of Ar, 40 l/h of O_2 and aerosol consumption 40 ml/h) we found partial pressure of CO_2 to be 2.1 mbar at total pressure 20 mbar. Corresponding T_{\min} was found to be 770°C. The experimental temperature of the phase appearance mentioned above is close to the estimated value. Our calculations show that the phase formation is very sensitive to the total deposition pressure variation. Thus the increase of the pressure up to 25 mbar (keeping the degree of oxidation constant) changes T_{\min} value for 795°C.

It is important that even in $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase stability field the presence of BaCO_3 as surface contamination is very possible. It was shown more than once that it leads to the weakening of intergranular links and decreasing of critical currents. The minor quantity of BaCO_3 is hard to detect by X-ray diffraction, evidently it is in the state of thin amorphous layers. Using Auger spectroscopy we confirmed some carbon contamination of the films obtained even at 920°C. According to ESCA data some part of carbon is really in the form of carbonate. Recently it was shown [8] that carbon contamination also constitutes a significant hindrance to oxygen diffusion in $\text{YBa}_2\text{Cu}_3\text{O}_x$ ceramics. We observed the similar effect when a 0.5 μm thick film deposited at 760°C was deficient in oxygen (judging by the *c* parameter equal to 1.176 nm) after cooling during 1 h in pure O_2 . An additional long time annealing (400°C, 6 h) was needed to reach full oxidation of the film (*c*= 1.167 nm).

4. Conclusions

To improve the quality of YBCO films prepared by low-pressure single aerosol source MOCVD as well

as to reach SC-phase formation at $T_d < 750^\circ\text{C}$ it is necessary to prevent BaCO_3 formation by reducing partial pressure of CO_2 in the deposition zone. The most effective ways are i) the increase of gas flow velocities, ii) the decrease of aerosol consumption with simultaneous increase of MOC concentration in the solution to maintain the rate of deposition. Both those factors will lead to lower degree of solvent oxidation advancement, more efficient escape of produced CO_2 , to lower heat evolution and consequently to better temperature control. The choice of appropriate solvent with low carbon content is also important. Among the solvents used diglyme is evidently the best.

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