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Studies of MOCVD for High T_c Thin Films

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Abstract: In this article we report on results obtained from studies of the effect of total pressure and carrier gas flow rate on the rate of precursor evaporation for typical precursors used in the MOCVD of high temperature superconductors (HTS). We find that this process is under significant mass transfer control and we consider the implications of this for growth of HTS. In particular, we discuss the problems associated with the use of solid precursors and possible strategies for solving the difficulties. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

After the discovery of high temperature superconductors (HTS) by Mueller and Bednorz in 1986[1] and the subsequent preparation a year later[2] of $YBa_2Cu_3O_{7-x}$ (YBCO) with a value of T_c above the b.p. of liquid nitrogen, the first article describing the preparation of thin films of YBCO by CVD appeared in 1988.[3] Subsequently, the discoveries of other HTS containing Bi, Sr, Ca and Cu (BSCCO) and Tl, Ba, Ca and Cu (TBCCO) in 1988 were rapidly followed by methods describing the CVD of these materials.[4,5] Since that time there have been more than 250 articles on the CVD of HTS materials.[6] The most potentially interesting application of HTS is in the field of microelectronics.[7] However, in order to build HTS devices it will be necessary to produce thin films of HTS by techniques which are compatible with fabrication lines, which allow close control of layer properties, which produce conformal thin films over large areas and have a high level of intra- and inter-sample uniformity, and which give a high sample throughput. CVD is just such a technique. The C in CVD emphasises that the technique is very dependent on precursor chemistry, deposition chemistry, and reaction parameters. This rapidly becomes apparent if one reviews results in the literature on the CVD of HTS when it is seen that a wide range of deposition conditions and layer properties have been reported.[6,8] Clearly the CVD of YBCO and other HTS, like many CVD processes, is a multiparameter problem, and much of what has been reported has been of an empirical nature. There is a need for understanding both precursor and deposition chemistry, as well as the effect of deposition parameters on layer properties. We have recently begun a programme of more basic studies of some of these topics[9–12] and in this article we consider factors affecting precursor transport to a CVD reactor.

2 EXPERIMENTAL

The experimental system and the conditions used have been described in detail elsewhere.[9,10] Briefly, the CVD reactor was an impinging jet system with a resistive heated substrate platform and standard gas handling facilities. The stainless steel precursor pot was also of a standard design. It consisted of two parts—a cylindrical body and a lid which was fitted with an inlet and an outlet for the gas flows. The lid and body were held together with six bolts and were sealed with a flexible graphite sheet between them. The inlet was fitted with a T-junction which allowed entry of a thermocouple through a Swagelock Ultratorrr fitting without obstructing the flow of the carrier gas. The gas inlet tube terminated 1–2 cm from the bottom of the container and the outlet tube only reached down about a third of the total container length. As just mentioned, this design of precursor pot is rather standard. For our experiments we added a small inner holder placed below the gas inlet.[13] This inner holder was normally filled with 1–2 g of precursor powder which had been compressed into a flat pellet in the base of the holder by using a plunger and a hydraulic press operated at a pressure of 3000 kg. The resulting 3–4 mm deep pellet in the base of the container was found to give a greater degree of reproducibility than when loose powder was used; this point is discussed further below. The inner container with the pellet was placed inside the sealed precursor pot with the tip of the sheathed thermocouple in contact with the top surface of the pellet. After being fitted to the gas handling system the pot was first evacuated and then flushed with argon after which the pot valves were closed ready for heating to be started. A period of 45–60 min was normally required to achieve a stable precursor temperature. The precursor pot was heated by circulating hot air in a temperature controlled enclosure.

Vapour generated in the pot was carried by a flow of argon through stainless steel gas lines either to exhaust or to the reactor; this flow was kept constant at 200 sccm except for a study of the effect of carrier gas flow on rate of precursor transport in which case it was varied between 25 and 400 sccm. The pressure in the precursor pot and reactor was measured with a Baratron capacitance gauge (0–100 Torr) and was controlled by throttling the pumping system. The total pressure was kept constant at 10 Torr except for the study of the effect of pressure (5–50 Torr) on rate of precursor transport. The precursor was mixed with O_2 (400 sccm) immediately before impinging on the heated substrate. The precursors reported on here are $Y(TMHD)_3$ and $Cu(TMHD)_2$ (where TMHD = 2,2,6,6-tetramethylheptane-3,5-dionate) and the temperature of the pot was kept at 108°C and 101°C, respectively. Deposition of films of either Y_2O_3 or CuO was typically undertaken at substrate temperatures corresponding to mixed kinetic and mass transport control.[13] Substrates used were Si(100) and film thickness profiles were measured by profilometry after lithographic etching with a mineral acid. Measurements of the quantity of precursor transported into the reactor were made by condensing the precursor in a cooled u-tube (weight approx. 20 g) attached to the end of the gas line at its entry point to the reactor. The u-tube was cooled with a mixture of dry ice and trichlorethylene (−60°C). The sublimation rate was determined by collecting the transported precursor for a known period of time and measuring the change in weight of the tube.

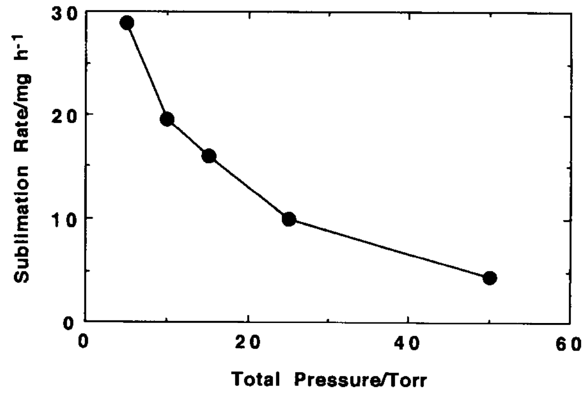

Fig. 1. Variation of $Y(TMHD)_3$ sublimation rate with total pressure.

3 RESULTS AND DISCUSSION

Figure 1 shows the variation of sublimation rate (Δm) with total pressure (P) for $Y(TMHD)_3$. From a plot of log Δm vs log P it is found that for P in the range $10 < P/\text{Torr} < 50$ there is a linear correlation (−0.99) and the variation can be represented by

$$\Delta m \propto P^{-0.93} \qquad (1)$$

Below 10 Torr the value of the exponent decreases rapidly. The observations for $P > 10$ Torr, together with a consideration of the design of the gas inlet nozzle to the vaporizer, suggest that there could be mass transport control of the precursor vapour. The gas inlet was such that the gas flow impinged directly on to the centre of the precursor pellet and it was noted that after use the majority of the precursor material had been removed uniformly from the region immediately under the exit of the nozzle. This is indicative of the behaviour of an impinging jet with a stagnation region.[14] The mass transport rate can be very simply represented by

$$\Delta m = k_m(C_s - C_b) \qquad (2)$$

where k_m is the overall mass transfer coefficient, C_s is the concentration of the precursor at the surface of the pellet and C_b is the concentration in the bulk of the gas phase. If, as is likely, $C_s >> C_b$ we obtain

$$\Delta m \approx (\text{Sh}/r)DC_s \qquad (3)$$

where Sh is the dimensionless Sherwood number and r is the nozzle radius. The Sherwood number is

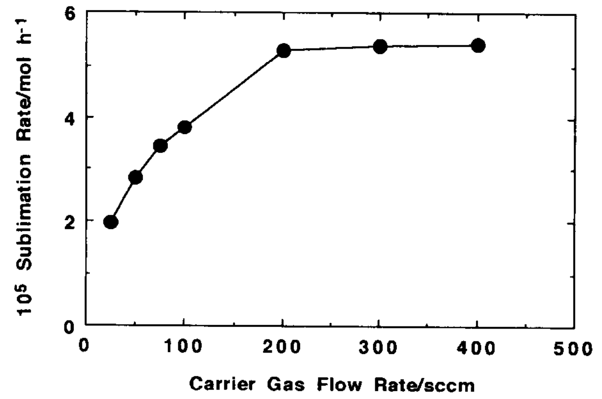

Fig. 2. Variation of $Cu(TMHD)_2$ sublimation rate with carrier gas flow rate.

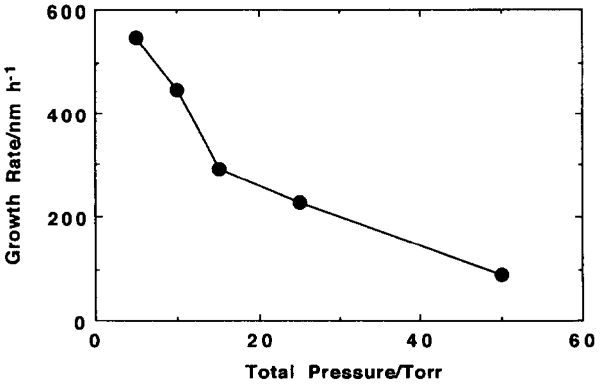

Fig. 3. Variation of growth rate of Y_2O_3 from $Y(TMHD)_3$ with total pressure.

the relation between the diffusion resistance based on a characteristic dimension of a body and the actual diffusion resistance; it can be shown[15] not to be strongly dependent on pressure under the operating conditions used. In contrast, D is inversely proportional to pressure, while C_s is determined by the vapour pressure of the precursor and not the total pressure. Hence

$$\Delta m \propto P^{-1} \qquad (4)$$

which is in reasonable agreement with the observed behaviour. Thus the very simple analysis given here suggests that the precursor evaporation rate is largely under mass transport control.

Further evidence of mass transfer control of precursor evaporation is given by results obtained for the effect of carrier gas flow rate on precursor sublimation rate at constant total pressure. Figure 2 shows this dependence for the vaporization of $Cu(TMHD)_2$. The sublimation rate is seen to increase for gas flows up to approx. 200 sccm and then to become almost constant. As discussed below, there was evidence that at the higher flow rates there was incomplete trapping of the precursor in the cooled u-tube and that in fact there should have been a continued steady increase in the sublimation rate with increased carrier gas flow rate. If mass transport is the rate determining process then using the relationship

$$\mathrm{Sh} = a\mathrm{Re}^b\mathrm{Sc}^c \qquad (5)$$

where a, b and c are constants and Re and Sc are the dimensionless Reynolds and Schmidt numbers, eqn (3) becomes

$$\Delta m = (a\mathrm{Re}^b\mathrm{Sc}^c/r)DC_s \qquad (6)$$

When only the gas flow rate is varying then this equation can be written in the form of

$$\Delta m \propto \mathrm{Re}^b \qquad (7)$$

The Reynolds number is defined as

$$\mathrm{Re} = ur/\nu \qquad (8)$$

where u is the linear gas velocity, r is the nozzle radius and ν is the gas kinematic viscosity. Hence, since the linear gas velocity is proportional to the volumetric flow rate (F) of the gas we have

$$\Delta m \propto F^b \qquad (9)$$

For the conditions in the precursor pot Re was always well below the critical value for turbulent flow and so the value of b in eqn (9) will be approx. 0.5.[16] The data from Fig. 2 in the form of a log–log plot give a linear correlation (0.998) and a slope of 0.47, which is in good agreement with the value expected from the simple mass transport model.

The evidence from the effect of total pressure and carrier gas flow rate on precursor sublimation rate means that vaporization will be very dependent on precursor pot geometry, as we have pointed out before.[11] So, from the point of view of deposition rates there will be a correspondingly marked influence of pot geometry. The close correlation between sublimation rates and deposition rates is seen when one examines the effect of pressure and gas flow rates on deposition rates. Figures 3 and 4 show these dependences and the close similarities to the variations in Figs 1 and 2, respectively, are apparent. A more quantitative comparison can be made for the effect of pressure by calculating the ratios of the data points at each given pressure. These are effectively constant with an average value of (20.5 ± 3.1) where the error is at the 95% confidence level. For the effect of carrier gas flow, the dependence of growth rate on gas flow rate when plotted in the form of a log–log

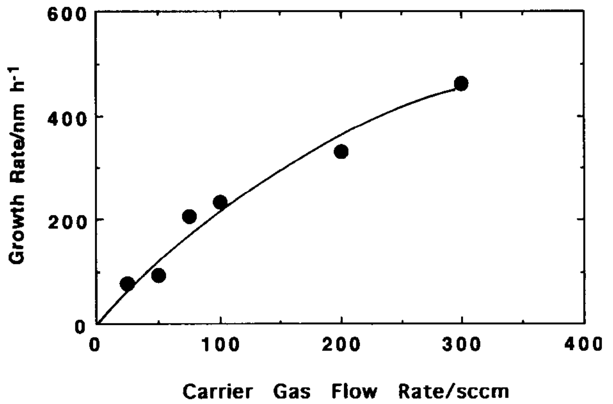

Fig. 4. Variation of growth rate of CuO from Cu(TMHD)$_2$ with carrier gas flow rate.

plot gives a straight line with a slope of 0.49, which again suggests mass transfer control of vapour transport from the precursor pot to the reactor. It can also be seen in Fig. 4 that the growth rate does not limit as gas flow rate increases, which indicates, as mentioned above, that there was incomplete trapping of the precursor in the cold trap at the higher gas flow rates.

As already mentioned, the design of the precursor pot used in this work is not an unusual one. The conclusions of this study may therefore be more widely applicable and, if this is the case, the fact that precursor transport is largely dependent on mass transfer in the precursor pot has an important general implication. That is, that precursor transport will also depend on the surface area of the precursor material exposed to the carrier gas. Now, if there are changes in crystalline structure of the precursor during repeated heating and cooling of the precursor pot between deposition runs then this could lead to changes in surface area and hence in the rate of precursor transport and, consequently, in the deposition rate. From X-ray studies of precursor material before and after use we have found that, indeed, morphological changes can occur,[17] and we have attributed a fall off in layer growth rate with usage time of precursor to slow annealing of the precursor in the pot and the resulting crystalline growth leading to an effective decrease in surface area exposed to the carrier gas. As mentioned in the Experimental section, we found that a compressed pellet gave more reproducible layer growth rates than when loose powder was used and this is probably because the formation of a compacted pellet helps to offset any changes in crystalline structure and surface area. Nevertheless, the effect can still be found to be present and we have seen this to be the case, for example, with growth of Y_2O_3 from Y(TMHD)$_3$.[12] These results emphasize the need for the possible development of a precursor delivery method capable of achieving stable and reproducible transport of precursor into the CVD reactor and/or the use of a technique for *in situ* monitoring and control of sublimation rates.[18] An alternative strategy which we have explored is to use precursors which are liquid under sublimation conditions. For example, we have reported[11] on a barium complex in which the t-butyl groups of TMHD have been replaced by C_3F_7 and in which the polyether, tetraglyme, has been introduced as an additional ligand to improve the volatility of the precursor. This has resulted in a complex which has a m.p. of 70°C, making it the most volatile and most stable barium precursor yet reported. A similar strategy has been employed for the production of an yttrium precursor where the complexing of the ligand 4-*tert*-butyl-pyridine-*N*-oxide with Y(TMHD)$_3$ has given a stable precursor with a m.p. of 97–100°C.[19]

4 CONCLUSIONS

The results presented in this article have shown that for typical solid precursors used in the preparation of HTS thin films by MOCVD the rate of vaporization and transport of the precursor from a standard container to the reactor is significantly controlled by mass transfer effects. This means that consideration has to be taken of changes in surface area of the precursor material which can give rise to changes in layer deposition rate under apparently identical conditions. These effects probably have contributed to the wide range of deposition results reported in the literature from the same precurcors. One solution we have suggested to the problem, and which we have reported on earlier,[11] is the development of precursors which are liquid at the sublimation temperature used.

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