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CONF-8910361--1

A Review of Metalorganic Chemical Vapor Deposition of High-Temperature Superconducting Thin Films

CONF-8910361--1

DE93 005147

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ABSTRACT

A status report is given on the metalorganic chemical vapor deposition (MOCVD) of high-temperature superconducting thin films. The advantages of MOCVD processing manifest themselves in the quality of the films produced, and in the economy of the process. Metalorganic precursor requirements, deposition parameters and film properties are discussed. Also difficulties have been identified in making MOCVD a manufacturing technology. To solve these problems, future research directions are proposed.

1. INTRODUCTION

The recent discovery of some oxide superconducting materials with transition temperatures above 77 K represent a major breakthrough for both science and technology.[1,2] But before these materials fulfill their promises, some processing techniques need to be developed to prepare these materials in the required shapes and sizes with high critical currents and high critical fields. These oxide superconducting materials are brittle and the physical properties are very process dependent. The brittleness issue can be addressed by using these materials in the form of either coatings or composites. The physical properties of these materials can be best controlled during the deposition by using a technique which allows the control of most of the thermodynamic variables during the growth.[3] The metal-organic chemical vapor deposition (MOCVD) technique is such a technique. This technique is currently the most important technique in the deposition of the compound thin films for electronics and optical device applications.

The advantages of MOCVD processing manifest themselves in the quality of the films produced, and in the economy of the process. Film characteristics such as conformal coverage and high purity, and processing benefits such as low temperature and radiation-damage free deposition, deposition selectivity and film stress and grain size control allow one to make unique, high quality films. At the same time, the high throughput and low cost per wafer associated with MOCVD processing make it very attractive economically.

FG05-86ER45266

In this paper, we review the status of the preparation of the high-temperature superconducting thin films by the MOCVD technique, and suggest future research directions for improvement.

2. DESCRIPTION OF THE MOCVD TECHNIQUE

In this growth process, one or more of the film constituents are transported to the reaction zone in the form of metalorganic compounds. The formation of the desired compound occurs via the pyrolysis of the metalorganics and the subsequent recombination of the atomic or molecular species at or near the heated substrate. The basic simplicity of the reaction and the gaseous nature of the reactants have established MOCVD as a useful epitaxial technology. The process can be well controlled by fixing the flow rates and thus the partial pressure of the various reactants with electronic mass flow controllers. Similarly, complex multilayer epitaxial structures are readily formed by exchanging one gas composition for another using automated gas-mixing systems. The pyrolytic nature of the reaction requires that only the substrates be heated to ensure efficient deposition, thus simplifying the temperature control.

Fig. 1 is a schematic diagram of the MOCVD system used for the deposition of the $YBa_2Cu_3O_{7-x}$ thin films.[4] The 2,2,6,6-tetramethyl-3,5-heptanedione (thd) compounds of Y, Ba, and Cu were used as the metalorganic precursors, which will be referred to as $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$. Each individual precursor source was placed in a separate stainless steel tube wrapped with heating tapes. An auxiliary outlet was introduced to avoid the deposition from the initial surge and unsteady gas flow. Argon was used as the carrier gas. By carefully controlling the gas flow rates and the source temperatures, the metalorganic precursors were evaporated and carried by argon gas to the reactor after premixing with oxygen gas. A warm-wall vertical reactor made of stainless steel was used with a resistive heating stage for the deposition.

3. MOCVD PRECURSORS

The nature of metalorganic compounds used to transport metals onto the surface of the substrate determines both the growth conditions and the properties of the films grown. A suitable precursor should have high enough vapor pressure for vapor transport; should not decompose at the operating temperatures losing its volatility; should be stable at room temperature for long term storage. For the deposition of superconducting oxide films, finding precursors satisfying the requirements above presents a challenge. So far, metal β-diketonates[5] have been used in the deposition of high-temperature superconducting films. These compounds are easy to handle because of their air-stability. However, they need to be heated to several hundred degrees centigrade to get high enough vapor pressure for transport, and they decompose at the precursor operating temperatures over an extended period. Other promising classes of compounds are some alkyl substituted cyclopentodienyl compounds developed at Georgia Tech. These compounds are liquid at room temperature and have much higher vapor pressures. Table I shows a list of metalorganic compounds which might be useful in the deposition of superconducting thin films.

4. MASS TRANSPORT STUDIES

Mass transport studies are important in the establishment of the MOCVD process parameters. Fig. 2 shows the mass transport rates as a function of carrier gas flow rates for $Cu(thd)_2$, $Ba(thd)_2$ and $Y(thd)_3$. The pressure was 50 torr on the sources and in the reactor with the Y and Cu compounds set at 160°C and the Ba compound set at 300°C. These experiments show that the mass transport rates are not very sensitive to the carrier gas flow rates for Y and Ba, but for Cu the mass transport increases strongly with increasing flow rate. Above 500 sccm, the mass transport is quite insensitive to a change in the flow rate even for Cu. It should be noted that we need a temperature for the Ba precursor which is almost double the temperature needed for Cu and Y to obtain a comparable mass transport. Fig. 3 shows the mass transport rates as a function of reactor pressure. Again, we note that the Ba and Y precursors do not vary much in the pressure range studied in comparison to the more rapid variation for Cu. Fig. 4 shows the mass transport rates in the log scale as a function of the inverse source temperature for the Y, Ba and Cu precursor at a reactor pressure of 50 torr. It is clear from the figure that the Cu and Y precursors are much more volatile in comparison to the Ba precursor and the order of this volatility for these three compounds follows the corresponding ionic radius quite well.[5]

In order to understand the deposition process further, we have carried out a systematic study of the mass transport for the precursors as a function of the deposition time. The results are shown in Fig. 5 (a) and (b). These experiments were performed with fixed conditions as follows, the reactor temperature at 600°C, pressure at 50 torr, gas flow rates at 500 sccm for Tl, Ba and at 85 sccm for Cu, Ca precursors. The metalorganic source temperatures were at 165, 160, 255 and 285°C for Tl, Cu, Ca and Ba precursors, respectively. All 4 components were run simultaneously. The starting chemical weights were at 0.5 grams for Cu and Ba, 0.6 grams for Tl and 0.4 grams for Ca, respectively. The transport time was started after the stabilization of the initial surge and unsteady gas flow. This should explain the zero offset in the figures. As can be seen, under deposition condition specified, the Cu and Ca precursors exhibit a linear behavior throughout the one-hour deposition time, while the data for Tl and Ba show a saturation after about 30 minutes. When the starting chemical weights are doubled, we have a linear behavior also for Tl and Ba as shown in Fig. 6(a) and (b). This suggests that in the first case most of the usable precursors were consumed within the first 30 minutes and the residue is just some involatile compound. These observations are consistent with the observation by Yamane et al.[6] that at a fixed evaporation temperature these compounds evaporate at a constant rate for the duration of several hours.

5. SUPERCONDUCTING THIN FILMS DEPOSITED BY MOCVD

The MOCVD technique has been used in the deposition of Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O thin films. Next, the results obtained so far for each class of compound will be reviewed.

5.1 Y-Ba-Cu-O films

Thin films of the $YBa_2Cu_3O_{7-x}$ compound have been deposited by using MOCVD by several research groups world-wide.[4,7-18] In the majority of the studies, $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ were used as the precursors. In few cases, fluorine-substituted β-diketonates have been used as the precursor, since they have higher vapor pressures.[14-16] However, these compounds require higher deposition temperatures in the presence of H_2O vapor to eliminate fluorine incorporation into the film. The superconducting thin films were obtained either by in-situ deposition, or by depositing the film at low temperatures (400-650°C) and by subsequent post-annealing in the temperature range 900-950°C. Fig. 7 shows the resistance as a function temperature for a film deposited at 650°C on yttria-stabilized zirconia (YSZ) and then post-annealed at 950°C under oxygen flow.[13] Growth rate was about 10 μm/hr and the film was c-axis oriented.

The in-situ deposition process uses lower deposition temperatures and produces very high quality c-axis oriented films. Deposition at low temperatures is important because it lowers the interdiffusion between the film and the substrate. The typical conditions for the in-situ deposition of $YBa_2Cu_3O_{7-x}$ is given in Table II. One of the most exciting things about the MOCVD technique is the very high critical current densities observed in the films grown by this technique.[17,19] The value of J_c is 4.1×10^5, 1.9×10^5, and 6.5×10^4 A/cm^2 at 2, 10, and 27 T, respectively.[19] Fig. 8 shows critical currents of a MOCVD grown film at 77.3 K and in magnetic fields up to 27 T.

5.2 Bi-Sr-Ca-Cu-O Films

Bi-Sr-Ca-Cu-O (BSCCO) films were prepared on MgO (100) single-crystal substrates by MOCVD using β-diketone compounds of Sr, Ca and Cu and Bismuth triethoxide or triphenylbismuth.[20-22] Table II gives the typical growth conditions for the growth of BSCCO. The films were c-axis oriented and the growth rates were in the range of 2-3 μm/h. The major phase was the $Bi_2(Sr,Ca)_3Cu_2O_x$, $T_c = 85$ K with some incorporation of the $Bi_2(Sr,Ca)_4Cu_3O_x$, $T_c = 110$ K phase. Four-point-probe measurements reveal the onset of film superconductivity at ~ 110 K and zero resistance at ~ 75 K. The SEM micrographs of the surface and cross section of the annealed films show flat and mica-like flakes overlapping.

5.3 Tl-Ca-Ba-Cu-O Films

The Tl-Ca-Ba-Cu-O film growth presents a challenge to the thin-film growers because of the high vapor pressure of Tl over the superconducting compounds. Since the MOCVD technique does not require a high vacuum, the volatility of thallium may be used as an advantage for the in-situ preparation of the Tl-based superconducting thin films. So far, however, the Tl-Ca-Ba-Cu-O thin films are obtained in the two steps. First the Ca-Ba-Cu-O films have been deposited at

600°C by using the β-diketone compounds of Ca, Ba, and Cu. Then, Tl-O is introduced in a sealed crucible at 800°C to achieve the superconducting phase.[23,24] Superconducting $Tl_2CaBa_2Cu_2O_x$ thin films have been successfully grown on the single crystal sapphire ($1\bar{1}02$) substrate by using the MOCVD technique without any intermediate buffer layer.[23] Fig. 9 shows the result of resistivity measurements as a function of temperature for a film deposited on sapphire ($1\bar{1}02$). Superconducting transition temperatures have been obtained with zero resistance at 94 K and 100 K for sapphire[23] and YSZ[24] substrates, respectively.

6. CONCLUSIONS

The MOCVD technique has been used to deposit $YBa_2Cu_3O_{7-x}$, Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O thin films with qualities comparable to those prepared by using the other techniques. Particularly, the critical currents under high magnetic fields in the $YBa_2Cu_3O_{7-x}$ films prepared by MOCVD are among the largest ever observed in oxide superconductors. However, at the present time, it is not clear whether MOCVD will be the technique for the production of oxide superconductors in large scale. This will depend largely on the development of new precursors with more volatility and stability, and the realization of in-situ deposition below 650°C. A systematic study is required to improve the β-diketonates known and to discover new classes of compounds. The plasma assisted MOCVD may be used to bring the deposition temperature below 650°C. Also, directed energy sources, such as lasers, may be used for depositing superconducting thin films selectively within the MOCVD reactor.

7. ACKNOWLEDGEMENTS

The authors would like to acknowledge helpful discussions with A. Zangwill and R. A. Young, and assistance from J. Cagle for the x-ray experiments. This work was sponsored by the Department of Energy. A. Erbil acknowledges an Alfred P. Sloan Research Fellowship.

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DISCLAIMER

Table I Some Metalorganic Compounds for the Deposition of Superconducting Thin Films by MOCVD (superscripts are reference numbers)

Compound	Melting Point(°C)	Vapor Pressure (mmHg)	Physical/Chemical Characteristics
$Ba(thd)_2$	172[25,27]	0.8 (220°C)	White cry. needles in EtOH, difficult to crystallize.
$Ca(thd)_2$	224[25,27]	1.1 (160°C)	White cry. needles in EtOH, difficult to crystallize.
$Cu(thd)_2$	201	0.5 (135°C)	Blue to purple cubic cry. in EtOH, ether, hexane, toluene.
$Sr(thd)_2$	200[25,27]		White cry. needles in EtOH or ether.
Tl(thd)	240	14.4 (165°C)	Light-yellow needles in EtOH or ether.
$Y(thd)_3$	168[26]	0.2 (135°C)	White cry. in EtOH.
$La(Cp)_3$	395[28]	1.4 (100°C)[29]	White cry. A.S.
$La(MeCp)_3$	155[28]		White cry. A.S.
$La(isopropylCp)_3$	< RT	1.5 (100°C)[29]	Light-yellow viscous liquid, A.S. dis. 170-220°C, 10 torr.
$CpCuP(Et)_3$	127[30]		White cry. needles, sub. 60°C , 5 torr.
$(EtCp)CuP(Et)_3$	< RT	3-4 (110-120°C)	Light-yellow/purple liquid, A.S.
$Y(Cp)_3$	295[28]	0.002 (100°C)[31]	Pale yellow cry. A.S.
$Y(isopropylCp)_3$	< 45		Light-yellow solid A.S. above RT, dis. 170-190°C,10 torr.
$Cu(fod)_2$	68	0.4 (100°C)[5]	Blue-green solid.
$Ba(fod)_2$	162		Yellow-white solid, dis. 200-220°C,5 torr.
$Y(fod)_3$	108[32]		Yellow-white solid dis. 200-220°C,5 torr.

thd=$C_{11}H_{19}O_2$, Cp=C_5H_5, MeCp=C_6H_7,
IsopropylCp=C_8H_{11}, Et=C_2H_5, fod=$C_{10}H_{10}O_2F_7$.
dis.=distill, sub.=sublime, A.S.=air sensitive, cry.=crystal,
EtOH=ethanol, RT=room temperature.

Table II. MOCVD Deposition Conditions[6]

	YBCO	BSCCO
Vaporizer Temperature	$Y(thd)_3$: 110-130°C $Ba(thd)_2$: 240-260°C $Cu(thd)_2$: 110-130°C	$Bi(C_2H_5O)_3$: 130-140°C $Sr(thd)_2$: 220-230°C $Ca(thd)_2$: 180-190°C $Cu(thd)_2$: 110-120°C
Deposition Temperature	800-900°C	770°C
Total Gas Pressure	10 Torr	1 Torr
Carrier Gas (Ar) Flow Rate	200 ml/min	200 ml/min
O_2 Gas Flow Rate	100 ml/min	100 ml/min
Deposition Time	1 hr	1 hr

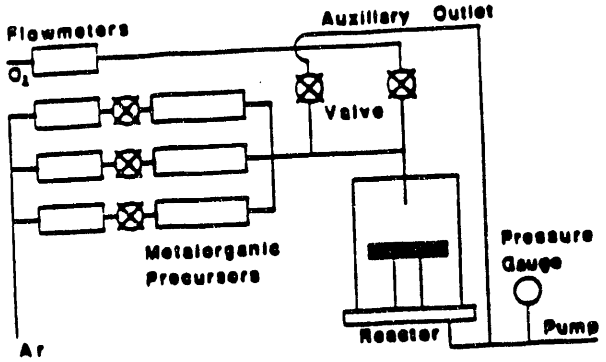

Figure 1. Schematic diagram of the metalorganic chemical vapor deposition system.[4]

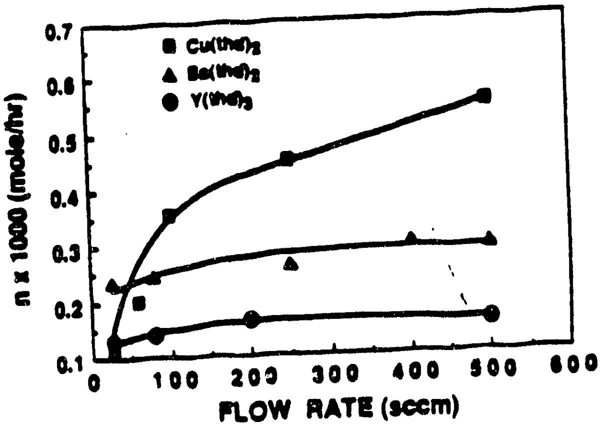

Figure 2. The mass transport rates as a function of carrier gas flow rates for various precursors with source temperature at 160°C for Y and Cu, 300°C for Ba.[4]

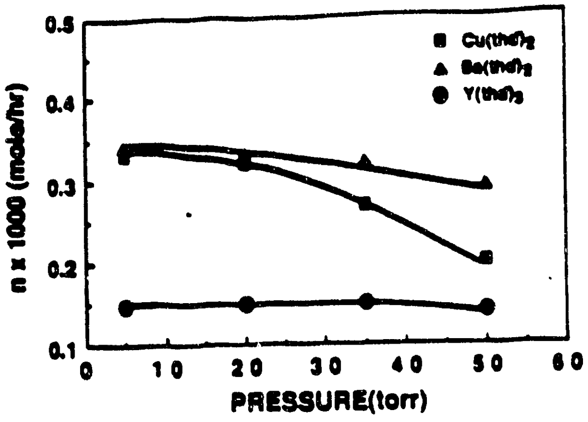

Figure 3. The mass transport rates as a function of the reactor pressure for various precursors with source temperature at 160°C for Y and Cu, 300°C for Ba.[4]

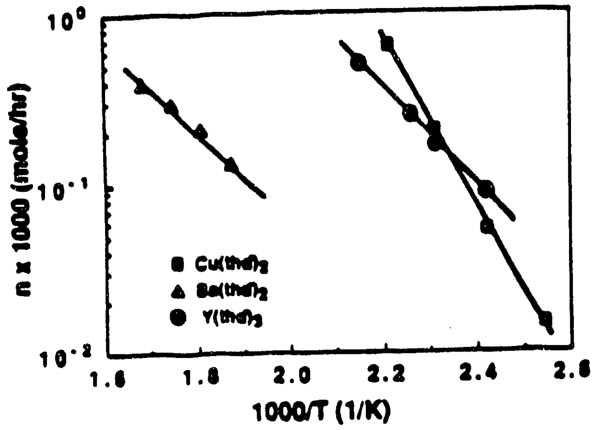

Figure 4. The mass transport rates as a function of the inverse source temperature for various precursors with reactor pressure at 50 torr, gas flow rates at 125 sccm for Y, 1000 sccm for Ba and 160 sccm for Cu.[4]

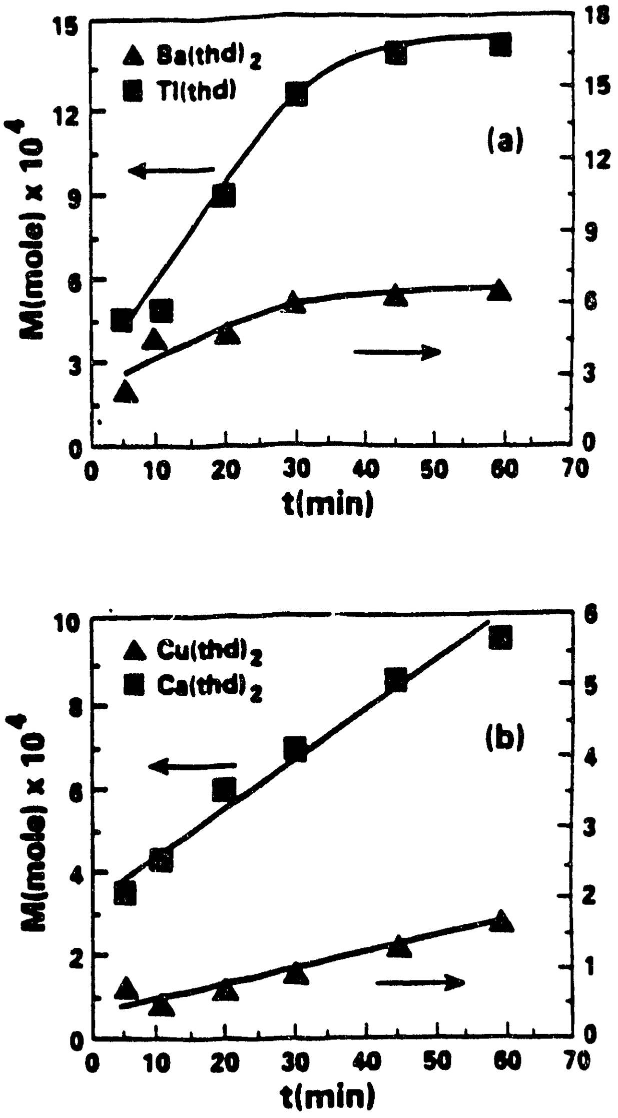

Figure 5. The mass transport as a function of deposition time for the metal precurcors of (a) Ba, Tl and (b) Cu, Ca with starting weights at 0.5 g for Cu, Ba, 0.6 g for Tl and 0.4 g for Ca.[23]

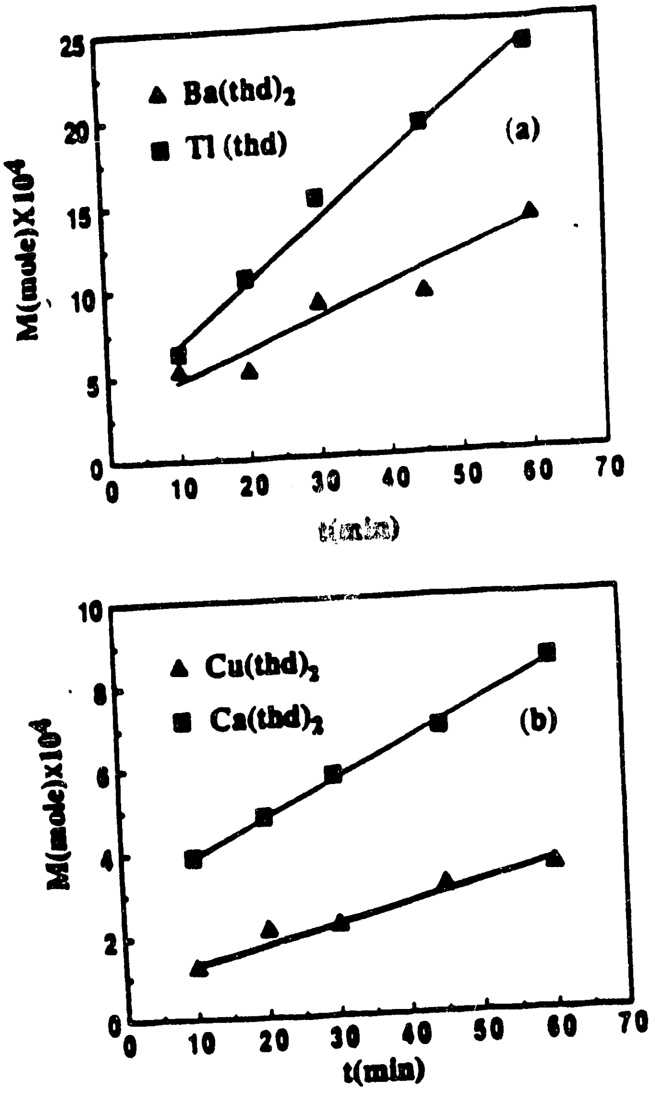

Figure 6. The mass transport as a function of deposition time for the metal precursors of (a) Ba, Tl and (b) Cu, Ca with starting weights at 1.0 g for Cu, Ba, 1.2 g for Tl and 0.8 g for Ca.

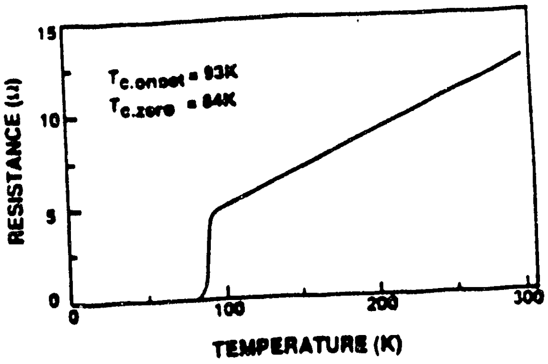

Figure 7. Resistance as a function of temperature for a post-annealed $YBa_2Cu_3O_{7-x}$ film deposited on YSZ.[13]

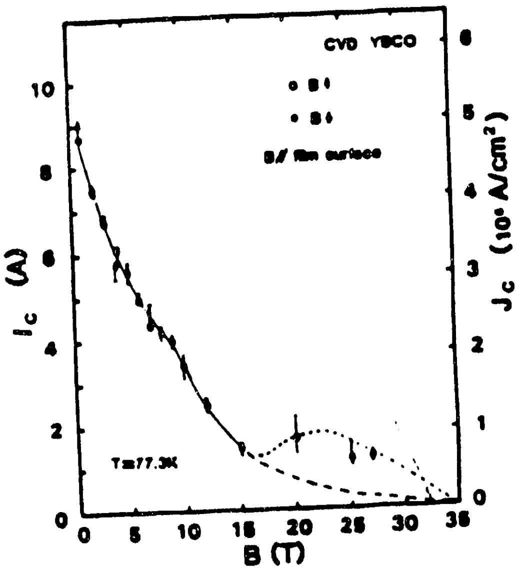

Figure 8. Magnetic field dependence of critical currents at 77.3 K up to 27 T for the thin film deposited by MOCVD technique.[19]

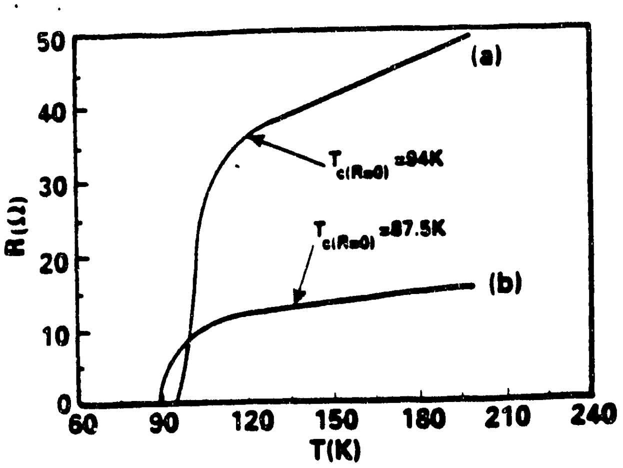

Figure 9. Resistance as a function of temperature for a $Tl_2CaBa_2Cu_2O_y$ thin film on sapphire post-annealed at 850°C in air for 40 min (b), and followed by further treatment at 500°C in O_2 for 6 hours (a).[23]

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