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STUDY OF THE PREPARATION OF HIGH T_c SUPERCONDUCTING YBCO THIN FILMS BY A PLASMA-ASSISTED MOCVD PROCESS

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Résumé Une méthode de CVD organométallique assistée par plasma a été développée pour préparer des films minces supraconducteurs (YBaCuO) à température inférieure à 400°C. L'étude préliminaire a montré que les films recuits "in situ" ou non recuits, ont une structure orthorhombique, de composition approximative $YBa_2Cu_3O_{7-x}$ sous certaines conditions. Dans le cas d'un film déposé sur un substrat en verre, une chute de résistance de 90% entre 110K et 77K a été obtenue. L'influence des paramètres de dépôt a été examinée.

Abstract- A plasma assisted MOCVD technique was developed to prepare Y-Ba-Cu-O superconducting thin films at low temperature, typically below 400°C. The preliminary result showed that the as-deposited or in situ plasma annealed films on a number of substrates exhibited orthorhombic structure, and of approximate $YBa_2Cu_3O_{7-x}$ composition under proper operating conditions. A resistance drop of 90% at 77 K with the onset above 110 K was obtained in a film deposited on glass substrate. The deposition behaviour and the influence of deposition parameters on the deposits were also examined.

The discovery of high T_c superconductivity in Perovskite-related oxides has sparked wide interests in preparing and studying thin films of these materials for both scientific and technological reasons. A variety of techniques, such as electron beam evaporation /1/, sputtering /2,3/, pulse laser deposition/4/, molecular beam epitaxy/5/ and chemical spray deposition/6/ etc. has been successfully employed to obtain superconducting thin films with zero resistance above 80 K. However, all these techniques have a common problem, i.e. an ex-situ post-annealing at high temperature, typically higher than 850°C, is required. This does not only limit the substrate choice within a few materials, such as SrTiO₃, YSZ, MgO and BaF₂, but sometimes also provides a poor surface morphology undesirable to device applications. Despite there was a report on sputtered films which were superconducting without post-annealing/3/, the substrate temperature was over 650°C, which is still too high to be compatible with the state of micro-electronic (say, IC) processing.

It is well known that metallorganic chemical vapor deposition(MOCVD) is currently the dominant techniques in the deposition of large-area device quality III-V and II-IV compounds with relative lower deposition temperature/7/. Furthermore, plasma-assisted CVD process has demonstrated substantially to lower the deposition temperature /8/. Just before the breakthrough of 90K high T_c superconducting oxides, we successfully prepared Yttria stabilized ZrO₂ (YSZ) thin films by using a plasma-MOCVD process at a substrate temperature below 200 °C /9/. Therefore, we have focused on the development of a similar process for synthesis of YBCO thin films. A tentative success was obtained in November, 1987 /10/.

The selection of precursor with suitable transport properties was the first step in concerning the deposition system. The experience in using beta-diketonates of Zr and Y for YSZ thin film/9/ enabled us to follow the same way. The copper acetylacetonate, $Cu(CH_3COCH_2COCH_3)_2$ [Cu(AA)₂] is known to be volatile/11/. The corresponding Yttrium acetylacetonate was reported to be

nonvolatile, whereas other Yttrium chelates with fluorinated and non-fluorinated groups substituting in the 1 and 3 position of the beta-diketone ligand were demonstrated as volatile at $150^{\circ}\text{C} - 250^{\circ}\text{C}$ /12/. In order to avoid possible undesirable side reaction from the presence of fluorine atoms, (as mentioned by Berry et al./13/) we choose the volatile Yttrium 2,2,6,6, tetramethyl-3,5-heptanedionate, $\text{Y}[\text{CH}_2\text{C}(\text{CH}_3)_2\text{COCOC}(\text{CH}_3)_2\text{CH}_3]_3$ [Y(DPM)₃] which was made in our lab./12/. The Ba precursor, $\text{Ba}(\text{DPM})_2$ was synthesized according to the same procedure. It was fortunately found to be remarkably volatile in reduced pressure system in our case, though it was reported to be nonvolatile under certain conditions/14/.

The deposition system is schematically shown in Fig.1. It consists of four chambers made of quartz. Three of them for individual metal precursor were wrapped with heating tapes to maintain at different temperature. A mixture of Ar and O_2 was used as both carrier gas and reactant (O_2). The deposition reactor was coupled with a radio frequency generator (13.56 MHz) for creating plasma (glow discharge) and the temperature was kept at about 300°C by a heat plate and infrared lamps. SrTiO_3 , YSZ, MgO, Sapphire, quartz and glass were tested as substrates. Some other operation parameters were:

r.f generator power: 100 w

substrate temperature: usually below 300°C

temperatures for sources: 150°C , 150°C and 250°C for
Cu, Y, and Ba, respectively

carrier gas flow rate: 10 - 20 sccs for each source

system pressure : approximately 2.0 torr

After deposition, and sometimes in situ plasma annealing, the deposition reactor was cooled down to room temperature under flowing pure atmospheric oxygen. During the introduction of different sources, we observed that the color of the plasma glow changed distinctly. This enable one to roughly estimate

how the deposition proceeds. The transport and deposition behaviour of each precursor source depends on the source temperature, carrier gas flow rate, substrate temperature, frequency and power of r.f. generator, Ar/ O_2 ratio of carrier gas, system pressure etc. Fig. 2 typically shows the relative contents of the three metals in the films deposited on substrates at different position away from the source location, analyzed by a plasma spectrometer. The three precursors obviously have different pyrolysis and deposition behaviour.

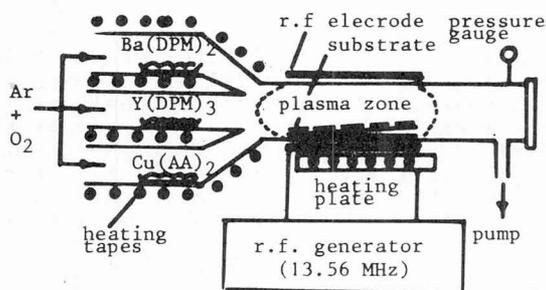


Fig.1 Schematic presentation of the plasma assisted MOCVD system for YBaCuO high Tc superconducting thin films.

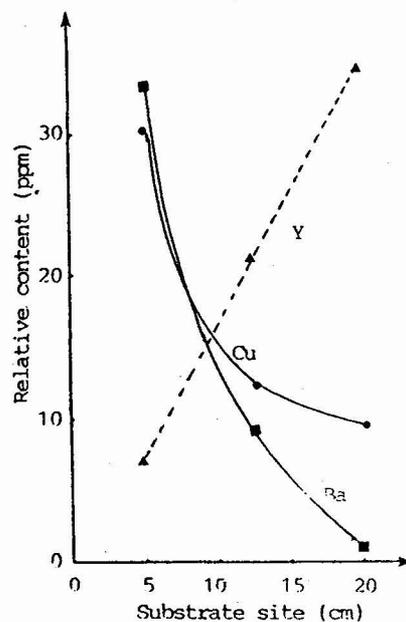


Fig.2 The relative contents of three metals in the films deposited at different position, showing their different deposition behaviour of the precursors.

The curves in Fig.2 indicated that most of Cu and Ba would be deposited out when they entrance the plasma zone, while the deposition of Yttrium showed a linear relation with substrate position which means that beta-diketone of Yttrium needs higher activation energy to perform deposition, compared with the former two. However, it is possible to adjust deposition parameters to get a right ratio for three metal elements in the growing layer, though it depends much on the feasibility of the design of CVD set up

Under proper operation conditions films could be obtained with rather smooth and bright surfaces, comparable to that of well polished substrate. The film thickness was within 0.2 - 1.0 μm in a deposition time of 30 to 60 min. Electrical measurement indicated that the films could be metallically conducting, semiconducting and insulating at room temperature

as was frequently reported before for bulk YBCO sintered bodies, due to poorly compositional control.

Fig. 3 is the XRD pattern of a film deposited on YSZ single crystal substrate. The appearance of strong peaks at the position for (013) (110) (103)

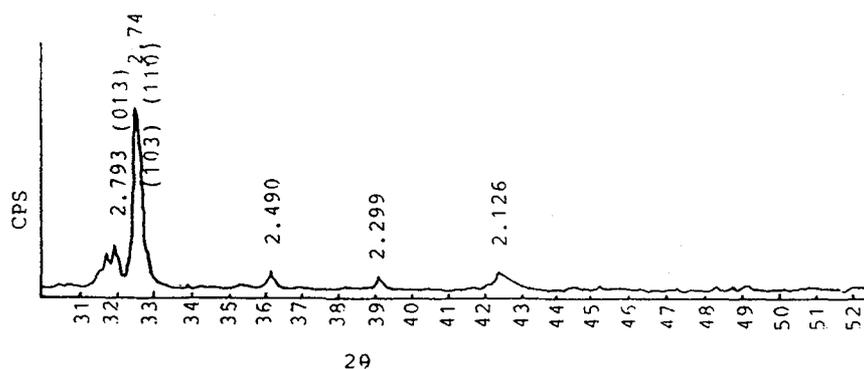


Fig.3 The XRD pattern of a YBCO thin film deposited on YSZ substrate.

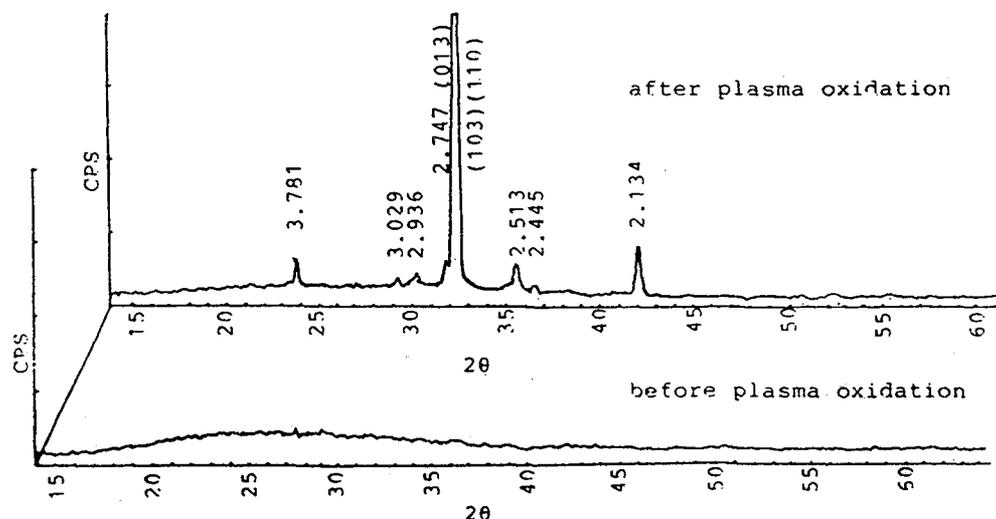


Fig.4 The XRD patterns of a YBCO thin film deposited on glass substrate, before and after plasma oxidation.

lanes of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ demonstrated the formation of this compound as a major phase and partially preferable orientation of the film, compared with the XRD pattern for bulk materials. The films deposited on amorphous (glass) substrates were usually amorphous. But it could be crystallized by in-situ plasma oxidation. Fig.4 illustrates this situation. As can be seen as-deposited film exhibited a typical amorphous XRD pattern, while after 60 min in-situ plasma treatment (only Ar/O_2 gas and without introducing source vapors) it showed strong (013)(103)(110) peaks of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase

Resistance measurements were carried out with a standard DC four probe technique in temperature range of 77K to 300K. Electrical contacts were made by pressing metal indium particles onto the film surface. Fig. 5 shows the R-T curve for the film mentioned above. It can be seen that the superconducting transition onset temperature is above 110 °C and resistance dropped 90 % down to 77-78 K. This behaviour did not change in several thermal cycles. However, the film lost its superconductivity after being exposed to air and re-making silver contacts for re-measurement with a more precise equipment in a liquid helium cryogenic system. This was certainly attributed to the instability of the superconducting phase to moisture, as indicated in many papers. Up to date we have not got a better sample, showing zero resistance at above 77K, mainly due to our poor CVD system, which was not able to be well adjustable. The work to set up a new system is in progress

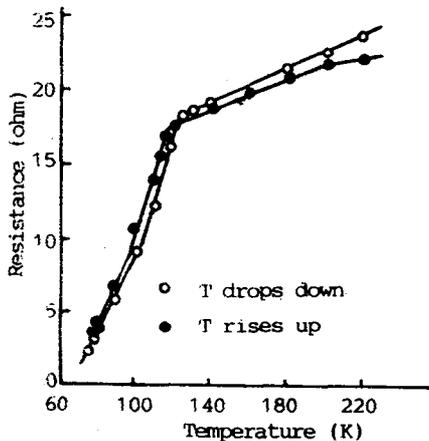


Fig.5 Resistance vs temperature curves for a thin film of YBaCuO by plasma-assisted MOCVD. (second thermal cycle)

Nevertheless, this preliminary result has proved the feasibility of preparing high T_c superconducting oxide thin films, including Y-Ba-Cu-O and possibly Bi-Sr-Ca-Cu-O or others, at really low temperature without need of an ex-situ high temperature post-annealing. Recently, there have been several reports on YBCO thin films by using MOCVD process^{13,15/}. In these works, the same kind of precursors, beta-diketonates of Y, Ba and Cu, were employed. However, the deposition temperature was no below than 650°C. And, the as deposited films were amorphous and a post-annealing (> 900 °C) was still necessary for obtaining superconductivity. As a matter of fact, the formation of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase with superconductivity is thermodynamically favourable in low temperature range. The plasma ambient provided sufficient activation energy to the reactant species for low temperature formation of this phase. Evidently, this was the right reason of the success in our case. It is believed that well developed CVD technology and control system would be able to make this plasma-assisted MOCVD process to be one of the most promising techniques for high T_c superconducting oxide thin films and even for large scale production of high T_c superconducting ribbons.

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