Single Liquid Source Plasma Enhanced Metalorganic Chemical Vapor Deposition of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films

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Submitted for Publication in

Applied Physics Letters

Advanced Technology Materials, Inc.
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July 29, 1992

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**REPORT DOCUMENTATION PAGE**

**REPORT DATE**
7/29/92

**REPORT TYPE AND DATES COVERED**
Technical report

**TITLE AND SUBTITLE**
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**ABSTRACT**
High quality YBa2Cu3O7-\(x\) films were grown in-situ on LaAlO3 (100) by a novel single liquid source plasma-enhanced metalorganic chemical vapor deposition process. The metalorganic complexes M(thd)\(_n\), (thd = 2,2,6,6-tetramethyl-3,5-heptanediolate; M = Y, Ba, Cu) were dissolved in an organic solution and injected into a vaporizer immediately upstream of the reactor inlet. The single liquid source technique dramatically simplifies current CVD processing and can significantly improve the process reproducibility. X-ray diffraction measurements indicated that single phase, highly c-axis oriented YBa2Cu3O7-\(x\) was formed in-situ at a substrate temperature 680 °C. The as-deposited films exhibited a mirror-like surface, had transition temperature \(T_c\) ≈ 89 K, \(\Delta T_c < 1 K\), and \(J_c(77K) = 10^6 A/cm^2\).

**SUBJECT TERMS**
Plasma enhanced metalorganic chemical vapor deposition, YBCO, superconductors

**ABSTRACT OF REPORT OF THIS PAGE**
Distribution Unlimited

**NUMBER OF PAGES**
12

**PRICE CODE**
N/A

**SECURITY CLASSIFICATION OF REPORT**
Unclassified

**SECURITY CLASSIFICATION OF THIS PAGE**
N/A

**SECURITY CLASSIFICATION OF ABSTRACT**
N/A

**LIMITATION OF ABSTRACT**
N/A
SINGLE LIQUID SOURCE PLASMA ENHANCED METALORGANIC CHEMICAL VAPOR DEPOSITION OF HIGH-QUALITY YBa2Cu3O7-x THIN FILMS

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ABSTRACT

High quality YBa2Cu3O7-x films were grown in-situ on LaAlO3 (100) by a novel single liquid source plasma-enhanced metalorganic chemical vapor deposition process. The metalorganic complexes M(thd)n, (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate; M = Y, Ba, Cu) were dissolved in an organic solution and injected into a vaporizer immediately upstream of the reactor inlet. The single liquid source technique dramatically simplifies current CVD processing and can significantly improve the process reproducibility. X-ray diffraction measurements indicated that single phase, highly c-axis oriented YBa2Cu3O7-x was formed in-situ at a substrate temperature 680 °C. The as-deposited films exhibited a mirror-like surface, had transition temperature Tc0 = 89 K, ΔTc < 1 K, and Jc(77K) = 10^6 A/cm².
Metalorganic chemical vapor deposition (MOCVD) has been shown to be a promising technique for the fabrication of device quality compound semiconductors and high-Tc superconducting thin films. Using MOCVD, films of the important classes of high-Tc superconductors have been deposited and shown to have properties comparable to thin films prepared by physical vapor deposition (PVD) techniques. In principle, CVD offers the advantages of high throughput, the capability of coating complex shapes, low equipment costs, and ease of scale-up to manufacturing volumes. However, the routine preparation of high-quality superconducting thin films by MOCVD has been impeded by the difficulties of reproducibly transporting the metalorganic precursors to the substrate. Standard delivery systems (bubblers) require the control of the temperature and flow rate for each precursor. The metalorganic precursors (especially the Ba precursor) currently used in the CVD preparation of high-Tc superconductors are not stable at the requisite sublimation temperatures, making accurate control of the film stoichiometry difficult over time. In this communication, we report a novel single liquid source MOCVD technique to prepare superconducting YBa$_2$Cu$_3$O$_{7-x}$ thin films. The single liquid source technique dramatically simplifies current CVD processing and can significantly improve the process reproducibility. The methodology reported here differs significantly from two other recently reported single source approaches.

YBa$_2$Cu$_3$O$_{7-x}$ films were grown in an inverted vertical reactor specially configured for the growth of complex oxides (Fig. 1). A rf plasma ($f = 13.56$ MHz, $P = 100$ W) was introduced to the deposition region in a down stream (remote) configuration. In this configuration, the plasma is generated far from the substrate and activated species are introduced into the deposition region through a quartz tube. The remote plasma configuration was selected to avoid pre-deposition gas phase reactions and ion bombardment of the surface of the films. A mixture of O$_2$ (flow rate = 500 sccm) and N$_2$O (flow rate = 250 sccm) was used as
the reactant gas. The total pressure of the reactor was 1.5 torr. The LaAlO$_3$ (100) substrates were held on a SiC susceptor which was heated by quartz-halogen lamps from the back surface. The substrate temperature was measured by a fine thermocouple in direct contact with the surface of the substrate.

The 8-diketonate complexes Y(thd)$_3$, Ba(thd)$_2$ and Cu(thd)$_2$ ($\text{thd} = 2,2,6,6$-tetramethyl-3,5-heptanedionate) were dissolved in a mixture of tetrahydrofuran (THF), isopropanol (IPA) and tetraglyme in a ratio of 8:2:1. The molarity of the solution was 0.40 mol/l. The film composition was controlled by varying the molar ratio of the complexes in the solution. The Y:Ba:Cu molar ratio in the solution was 1:4:4. THF was chosen as a solvent because of its large solubility and compatibility with the precursors. IPA and tetraglyme were added to lower the evaporation rate of the solution and increase the stability of Ba(thd)$_2$ during evaporation. The solution was injected by a liquid pump into a heated, stainless steel vaporizer which was maintained at 230 °C during the deposition (Fig. 1). The transport rate of the solution to the vaporizer was 3 -6 mm$^3$/min. The precursor vapor was carried upstream of the reactor inlet by nitrogen carrier gas (flow rate = 50 sccm) and the vaporization process takes place on a continuous basis. The deposition rates were 0.2 - 0.5 μm/hr and the typical film thickness was 0.3 -0.5 μm, although continuous films as thin as 0.1 μm have been deposited.

To complete YBa$_2$Cu$_3$O$_{7-x}$ film oxidation, the deposition chamber was backfilled to ~ 100 Torr with oxygen gas while the substrates were slowly cooled to room temperature at a rate 10 °C /min. The composition of the films was measured by energy dispersive X-ray analysis (EDX). The standard deviations of the Y, Cu, and Ba atomic ratios determined by the EDX analysis were 1.6, 3.7, and 4.4 percent, respectively, indicating the single liquid source technique yields reproducible results. The deposition reproducibility is achieved because the source reagents in the single liquid source technique are at their vaporization
temperature for a very short time rather than the entire time of the deposition run; consequently the partial pressure of all the source reagents remain constant during growth. High quality superconducting films were found to be consistently Ba deficient and Cu rich which is consistent with a recent report by Zhao et al.11

The microstructure of the films was characterized by XRD using Ni-filtered Cu Kα radiation. Fig. 2 shows the X-ray diffraction pattern for a typical YBa2Cu3O7-x film deposited at 680 °C by PE-MOCVD. As can be seen from the figure, single phase, highly c-axis oriented YBa2Cu3O7-x was formed by single liquid source PE-MOCVD. The c-axis repeat distance derived from the (001) x-ray peaks is 11.68-11.69 Å, corresponding to YBa2Cu3O7-x with nearly complete oxidation (x < 0.1).12 Rocking curves obtained from the YBa2Cu3O7-x (005) reflection displayed a full width at half maximum as low as 0.32°. The as-deposited films were smooth and exhibited a mirror-like surface. Scanning electron micrographs of two YBa2Cu3O7-x films, one 0.1 μm thick (Fig. 3a), and another 0.4 μm thick (Fig. 3b) both indicated the formation of continuous dense material. The particulates scattered on the film surface are typical of YBa2Cu3O7-x films grown by MOCVD.13,14 It is noteworthy that there are significantly more particulates scattered on the surface of 0.4 μm thick film than the 0.1 μm thick film. Similar observations have also been made recently by DeSisto et al for their YBa2Cu3O7-x films prepared by MOCVD.14

The superconducting properties of our YBa2Cu3O7-x films were characterized by both inductive and four point probe resistivity measurements. Fig. 4 shows the relative inductance change of an in-situ YBa2Cu3O7-x film measured using a Lakeshore screening system. The sharp transition in the inductance data indicates that the film is nearly single phase YBa2Cu3O7-x with a Tc = 89.5 K and ΔTc = 0.4 K. The electrical resistivity ρ was measured using a four point probe technique. Typical ρ(T) results show that ρ decreases nearly
linearly with T until the film enters the superconducting state at $T_{c0} = 89$ K. Measurements of the critical current density $J_c$ were carried out by both dc susceptibility and transport techniques. Susceptibility measurements show that the $J_c (77 \text{ K}) = 10^6 \text{ A/cm}^2$. Transport measurements of $J_c$ were carried out using a 1.2 cm long, 10 µm wide transmission line. These measurements yield a $J_c (77 \text{ K}) = 3.3 \times 10^5 \text{ A/cm}^2$ using the 1 µV/cm criterion.

In summary, our results show that high-quality superconducting YBa$_2$Cu$_3$O$_{7-x}$ were prepared in-situ on (100) LaAlO$_3$ by a novel single liquid source plasma-enhanced metalorganic chemical vapor deposition process at a substrate temperature of 680 °C. The single liquid source process dramatically simplifies current CVD processing and can significantly improve the process reproducibility. Both four probe resistivity and inductive measurements revealed that the as-deposited YBa$_2$Cu$_3$O$_{7-x}$ films have superconducting transition temperature $T_{c0} \equiv 89$ K and $\Delta T_c < 1$ K. Critical current densities $J_c$ at 77 K derived from magnetic measurement was $10^6 \text{ A/cm}^2$. A 1.2 cm long, 10 µm wide YBa$_2$Cu$_3$O$_{7-x}$ transmission line yielded a $J_c = 3.3 \times 10^5 \text{ A/cm}^2$ at 77 K.

The authors would like to thank Mark A. Stan and David Davis of NASA Lewis Research center for the magnetic $J_c$ measurements of our YBa$_2$Cu$_3$O$_{7-x}$ films. The authors would also like to thank Guang-Ji Cui for useful discussions. This research was supported by the National Aeronautics and Space Administration under contract NAS3-25932. The initial development of the liquid delivery system was partially supported by DARPA under contract N00014-90-C-0201.
REFERENCES:


Figure captions:

Fig. 1 Schematic diagram of single liquid source CVD reactor.

Fig. 2 X-ray diffraction pattern for a typical YBa2Cu3O7-x film on LaAlO3 (100) substrate by single liquid source PE-MOCVD.

Fig. 3 Scanning Electron Micrographs of YBa2Cu3O7-x films on LaAlO3 (100) substrate by single liquid source PE-MOCVD; (a) 0.1 μm thick. (b) 0.4 μm thick.

Fig. 4 Inductive measurement data for a typical YBa2Cu3O7-x film on LaAlO3 (100) substrate by single liquid source PE-MOCVD.