Vaporization of a Mixed Precursors in Chemical Vapor Deposition for YBCO Films

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Abstract

Single phase $YBa_2Cu_3O_{7-\delta}$ thin films with T_c values around 90 K are readily obtained by using a single source chemical vapor deposition technique with a normal precursor mass transport. The quality of the films is controlled by adjusting the carrier gas flow rate and the precursor feed rate.

* Key words: MOCVD, YBCO Thin films, mixed precursor

Typeset using REVTEX

1. INTRODUCTION

Metalorganic chemical vapor deposition (MOCVD) has been used for preparing high T_c superconducting (HTSC) thin films. The technique is appealing because only the susceptor holding the substrate need be at high temperatures (800-900°C). The remainder of the reactor, including the precursor sources are at much lower temperatures, usually less than 300°C. The precursors used in MOCVD preparation of HTSC oxide thin films are most frequently metal beta-diketonates. High T_c superconductors as multi-component oxides require more than one component source with each source containing different precursors. The volatility and stability of the precursor strongly depend on temperature, system pressure and carrier gas flow rate. All effects of these system conditions are interdependent. They have to be carefully controlled for each individual source in a conventional multisource MOCVD system in order to achieve the appropriate gas phase composition and ultimate proper elemental stoichiometry in the film. In order to circumvent the operational problems associated with the multisource MOCVD system, a mixed precursor single source system has been developed which employs a specially designed mixed precursor vaporizer [1,2,3]. We discuss here the vaporizing characterization of the mixed precursor and its effect for YBCO films.

2. EXPERIMENT

The MOCVD apparatus consists of a precursor vaporizer made of pyrex glass and a quartz reactor [2]. The vaporizer has four principal components, as shown in Fig. 1a. They are a tubular housing, A, a 25 mm O.D. standard wall, slotted glass tube, B, a high intensity quartz halogen light bulb (heater), C, and a motor driven screw conveyor, not shown. The housing is equipped with a water jacketed cooling section, D, and a narrowed section, E, of 10 mm O.D. tubing, to which the heater is adjacent. The tube's cross section has the shape of the letter "C" (Fig. 1b). The upper section of the slotted tube is unmodified tubing and is inserted into a receiving hole in the base of a fluted "pinion shaped" teflon plug, F and Fig. 1c. At the center of the teflon plug is a button-shaped neodymium magnet, H. The plug, which can move freely up and down within the 25 mm O.D. section of the housing, is magnetically coupled to a second neodymium magnet affixed to the screw conveyor.

The precursors for the YBCO films are diketonate of $Y(thd)_3$, $Ba(thd)_2.OH.2H_2O$ and $Cu(thd)_2$. A mixture of powders of these precursors, in the ratio of, or close to, Y: Ba: Cu =1: 2: 3, is loaded into the slotted section of the tube with vibration to facilitate compaction. During operation of the vaporizer, the screw conveyer slowly advances the slotted

tube through the cooling section and into the heated section serviced by the lamp. Upon exposure to the light source, the mixed precursors are vaporized. Because the teflon plug is fluted, carrier gas (e.g., Ar), can flow freely past the plug to sweep vaporized precursors out of the heated section towards a susceptor for deposition at a pressure of 5 - 7 torr. With this design, the precursors are kept relatively cool throughout their movement in the vaporizer until they are flash heated and vaporized in the heated section. The typical growing conditions have been described elsewhere [2].

3. RESULTS and DISCUSSIONS

As seen from the sketch of the apparatus shown in Fig. 1, the usual arrangement is to have the charged slotted tube move vertically downward through the short heating zone. Experiments indicated that for every individual component beta-diketonate powder, the vaporization process was quite regular. At a proper power range (150-250 watts) for the heating lamp, an asymmetric curved surface of the organometallic powder compact was established and the length of the part within the heated zone depended on the precursor advancing velocity [2].

In order to maintain proper stoichiometry of vapor carried downstream

from the heating zone, it is imperative that each of the components of the premixed powder which enters the heating zone be evaporated by the time the mixture traverses the heating zone. During the travel through the heating zone, the precursor melt develops an asymmetric curved surface, which can be either convex or concave, depending upon the orientation of the slot in the tube with respect to the heating lamp. The shape and the length of the melt wedge are functions of the feed rate of the slotted tube into the heated zone. With a melt composed of mixed precursors, it is likely inhomogeneities will exist (as the following experiments indicated). Along the length of the melt, the leading section will be rich in the least volatile (highest vaporization temperature or lowest vapor pressure) component, as the more volatile component(s) will have been vaporized to a greater extent. Each succeeding section, going backwards towards the unmelted mixed precursors, will have a higher proportion of the lower melting point /higher vapor pressure component(s). It has been proposed theoretically [3] that once a steady state equilibrium melted phase with a non time varying composition has been established, then the precursor vapors emerging from the heating zone will have a mole ratio equivalent to the mole ratio of the solid mixture. This allows for non stoichiometric concentration gradients in the melted phase so long as these remain in steady state equilibrium.

If the precursors are exposed to air (moisture), its vaporization and mass transport turned out to be rather poor. The barium beta-diketonate

after absorbing moisture runs down the tube as a yellow liquid, which afterwards leaves a black deposit (the Ba is identified by EDAX) on the walls. A reduction of the Ba content leads to a nonstoichiometric gas phase and deposited film. This can be seen in X-ray diffraction patterns of such a film shown in Fig. 2a. EDAX show that the film lacks in Barium (Cu:Ba = 75:1.5). XRD patterns identify the peaks in Fig.2b to be the (002), (004), (006) and (008) reflection from oriented $Y_2Cu_2O_5$.

The precursor vaporization can be improved by adjusting the carrier gas rate and the precursor feed rate. A larger flow rate and lower feeding velocity favors precursor vaporization. For a poor precursor source the preparation of a mixed precursor with more barium content would be a solution. For instance, an argon gas flow rate of 300 sccm (standard cc/min) and 0.3 mm/min of feeding velocity, using a precursor of Y:Ba:Cu = 1:2.2 :3 resulted in an almost pure 123 phase film with perfect (001) orientation on MgO (200) substrate (Fig. 2b). This sample showed a superconducting transition above 90 K with a zero resistance temperature higher than 85 K.[2] It was found that if the mixed precursor was newly prepared in a dry glove box filled with ultra dry nitrogen or helium, the precursor could be transported completely by argon gas with in an even lower flow rate (< 150 sccm). Under these operating conditions the YBCO thin films of almost pure $YBa_2Cu_3O_{7-\delta}$ phase on various substrates have been reproduced.

4. CONCLUSIONS

A simple source MOCVD system has been developed. The vaporization is a function of the feeding velocity and carrier gas flow rate. The key point to obtain good composition control was to keep the precursor absolutely dry. Precursor vaporization can be improved by adjusting the carrier gas flow rate and the precursor feed rate and $YBa_2Cu_3O_{7-\delta}$ thin films on YSZ (200) and MgO (200) substrates were readily obtained.

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FIGURE CAPTIONS

Figure 1. (a) Schematic diagram of the vaporizer of a single mixed precursor

(b) the slotted glass tube.

(c) the fluted "pinion shaped" teflon plug.

Figure 2. XRD patterns of YBCO thin films.

(a) A perfect (002) oriented $Y_2Cu_2O_5$ thin film with Ba deficiency in precursor transport.

(b) (001) oriented 123 phase film, deposited with improved precursor mass transport.

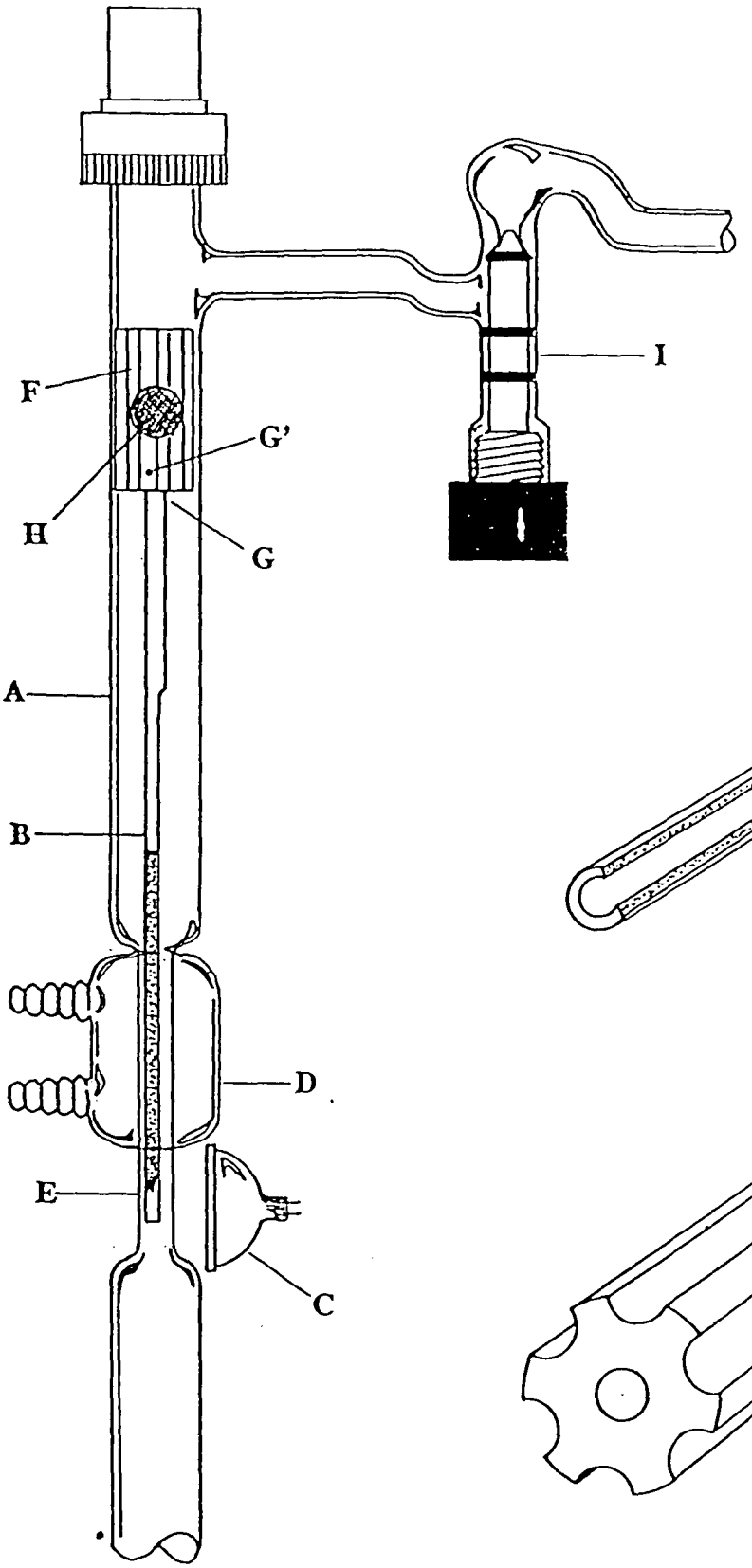


Fig. 1a

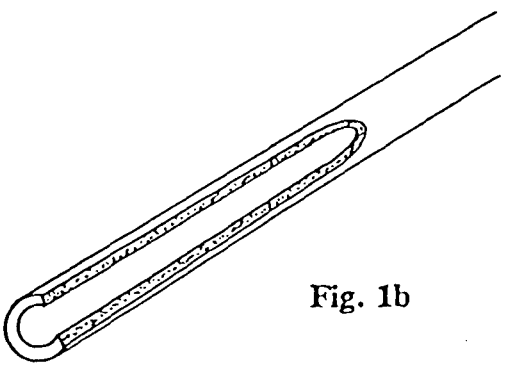
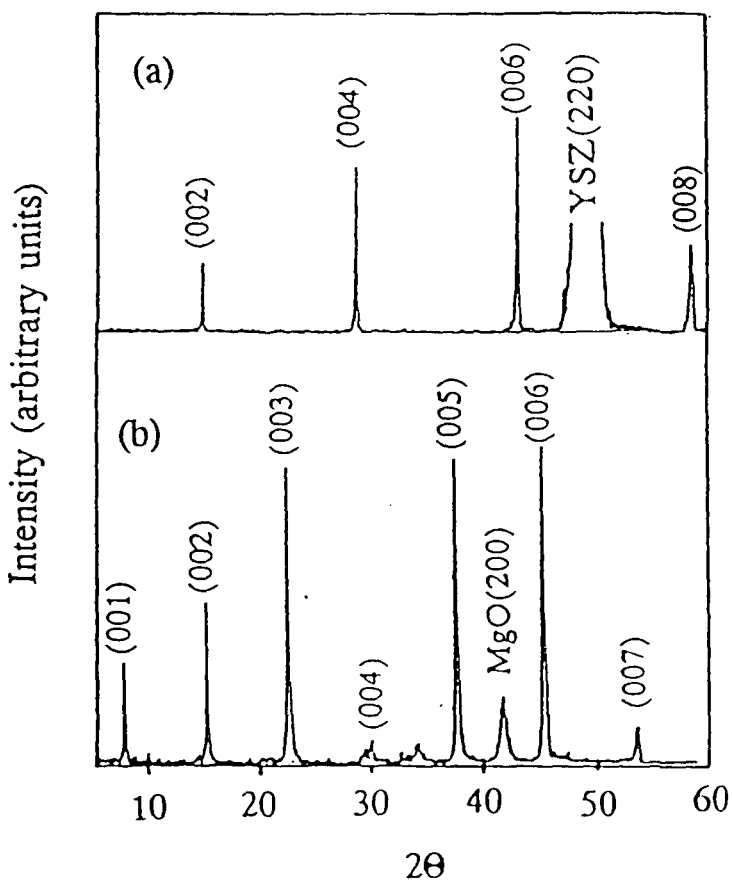


Fig. 1b

Fig. 1c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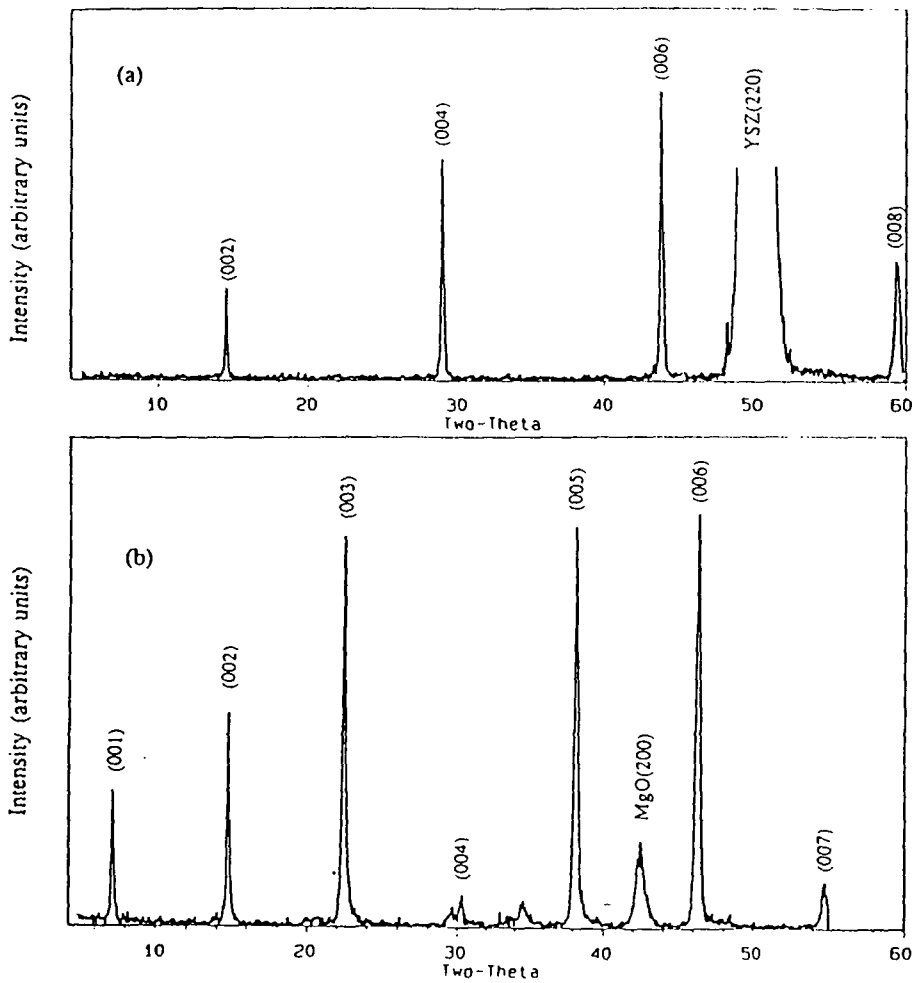
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