

# Trajectory-property relationships in MOD-derived YBCO films

D.E. Wesolowski, M. Yoshizumi, M.J. Cima \*

Massachusetts Institute of Technology, 77 Massachusetts Ave #12-011, Cambridge, MA 02139, United States

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## Abstract

A study of the physical and chemical changes during processing in MOD-derived YBCO films was performed. Fully processed films were 70–85% of theoretical density. The sintering rate increased substantially in the compositional range F/Ba = 1.8–1.5. The activation energy for sintering decreased above a P(H<sub>2</sub>O) dependent threshold temperature. XRD indicated this temperature/composition threshold also corresponded to YBCO nucleation, suggesting *ex situ* YBCO forms in contact with a melt. The ramp rate and P(H<sub>2</sub>O) were used to control F/Ba trajectories, which were correlated to performance. The nucleation of YBCO was strongly dependent on processing conditions. Nucleation temperature was varied by at least 60 °C in the study. The optimal YBCO nucleation temperature in the 300–800 nm films was around 725 °C. *a*-axis grains dominated the microstructures of films where YBCO nucleated at <700 °C. Large second phases, but no *a*-axis grains, were found when the nucleation temperature was >750 °C.

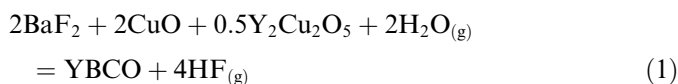
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## 1. Introduction

Metal-organic deposition (MOD) is a proven method for the preparation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) thin-films and is used in pilot scale production of coated conductors [1]. The mechanism by which precursor film is converted to YBCO has, however, never been fully described due to the complexity of the process. The following overall reaction has been suggested:



Reaction (1) does not describe a specific reaction in the system, but rather the overall conversion of precursors to the YBCO product. This reaction occurs in steps during heat treatment [2,3]. Recent investigations have suggested that reaction (1) poorly represents the actual conversion pro-

cess. The overall fluorine-to-barium (F/Ba) ratio of films provides insight into the compositional changes that occur during processing. F/Ba ratio measurements by Yoshizumi, et al. showed that precursor films following decomposition have about three times as much fluorine in the film as barium (F/Ba ~ 3), indicating some fluorine is bound in the film as YF<sub>3</sub> [2].

MOD precursor films undergo significant chemical changes before YBCO nucleates. Analysis of F/Ba ratio and P(HF) over the film during processing has revealed the decomposition of fluorides occurs in steps. YF<sub>3</sub> is thermodynamically less stable than BaF<sub>2</sub> and decomposes completely before BaF<sub>2</sub> decomposition begins. YF<sub>3</sub> decomposition results in removal of Y from a BaF<sub>2</sub> solid solution [2]. The decomposition product is unknown, but Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> phase is detected in XRD just before nucleation of YBCO [2]. Y<sub>2</sub>O<sub>3</sub>, Y(OH)<sub>3</sub> [4], and yttrium oxyfluoride [5] have also been proposed as reaction products. BaF<sub>2</sub> begins to decompose without the formation of YBCO [2]. A number of reactions could possibly represent BaF<sub>2</sub> decomposition in the region of 2.0 > F/Ba > ~1.5. The most likely, as estimated

\* Corresponding author. Tel.: +1 617 253 6877; fax: +1 617 258 6936.  
E-mail address: [mjcima@mit.edu](mailto:mjcima@mit.edu) (M.J. Cima).

from P(HF) measurements, is the formation of BaCuO<sub>2</sub> [2]. A Ba(O<sub>x</sub>F<sub>y</sub>) superstructure has been detected in e-beam derived films, and may form in MOD films as well [6,7].

A transient liquid phase is speculated to exist during processing of *ex situ* films. Crystallites of BaF<sub>2</sub> phase material of up to 20 nm have been observed in TEM images of films quenched near the nucleation of YBCO, and these crystallites actually grow during heating as more Y is removed from solution [8]. Growth rates of YBCO, however, exceed 5 nm/s [9]. The large chemical inhomogeneity in precursor films indicates a phase with high cation mobility, such as a melt, is necessary to obtain the required growth rates. The chemical makeup or even the presence of a melt has never been established. McIntyre proposed the presence of a cuprate melt, some of which are known to exist at low-temperatures and have a P(O<sub>2</sub>) dependence [8]. Yoshizumi, et al. noted the additional fluorine in MOD-films could promote transient fluorine-rich melts during processing [2]. Solovyov, et al., while working with e-beam derived BaF<sub>2</sub> containing films, found a fluorine-free amorphous layer at the YBCO growth interface [10]. It was suggested that this was a quenched fluorine-free melt [4].

The study of physical changes in *ex situ* films has been mostly limited to microstructure studies. Thickness changes of MOD-derived films were monitored in this study during high-temperature processing. Cross-sectional SEM studies have previously shown shrinkages in excess of 50% from decomposed to final film thicknesses [9,11]. Other researchers have suggested this is due to the presence of porosity in the decomposed film [8]. TEM and XRD studies of the films have shown that the decomposed films are nanocrystalline in nature, consisting of small crystals of BaF<sub>2</sub> and Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> in a mostly amorphous and porous matrix [9,8]. The small particle size in the precursor film and the initial porosity means there is a large driving force for shrinkage by sintering. Shrinkage also occurs because film fluorine is replaced with half as much oxygen during conversion. The solid products of Reaction (1) have a 20% smaller volume than the solid reactants. Small thickness changes occur due to substrate reactions [12]. Sintering and conversion should account for most film thickness change.

Physical and chemical changes in MOD-derived films during ramping and annealing are reported in this paper. The physical changes observed included the change in film thickness and surface morphology of the films. The overall F/Ba compositional trajectory of the films and XRD phase relations were used to deduce chemical changes. Comparisons between physical and chemical changes were used to infer the presence of a fluorine-free melt that is associated with the nucleation and growth of YBCO. The relationships between trajectories and performance were explored.

## 2. Experimental

Samples were prepared according to well-described procedures for the production of MOD YBCO [11]. Solutions

of two different concentrations were used to provide films of two thicknesses following decomposition (~1.1 μm and ~0.7 μm). The higher concentration solution was prepared by allowing solvent to evaporate from the more dilute solution. Several substrates were used, including bare (100) aligned Zr<sub>0.87</sub>Y<sub>0.13</sub>O<sub>2</sub> (YSZ), YSZ coated with solution-deposited epitaxial CeO<sub>2</sub>, and bare (110) aligned LaAlO<sub>3</sub> (LAO). Details of the solution deposition process for epitaxial CeO<sub>2</sub> can be found elsewhere [13]. Samples were cleaned before spin-coating and coating was performed for 120 s at 2000 rpm (for thick films) or 4000 rpm (for thin films) in a particle containment hood. A low-temperature heat treatment described elsewhere [11] was used to decompose samples following this spin-coating.

The edges of the samples were removed after decomposition using a razor blade. Film areas following edge removal were on average  $5.32 \times 10^7 \mu\text{m}^2 \pm 6\%$ , or approximately 7.5 mm × 7.5 mm. Bridges were also scribed with a razor blade into samples designated for current testing. Debris from film removal was removed using a jet of dry nitrogen.

Film thickness measurements were performed using a Tencor P10 profilometer. Six measurements were performed on each sample, two in the center of the edges and four closer to each corner. Profilometer measurements were taken at a rate of 100 Hz and speed of 20 μm/s, giving an approximate spacing of 200 nm between measurements. Typical scan lengths were ~700 μm with 100–300 μm on the film itself. The starting corner for the thickness measurement was marked with a scratch in the film so approximately the same positions could be measured after the high-temperature heat treatment. The profilometer accuracy was checked by testing a VLSI thickness standard of 4500 Å over the whole range of dates relevant to this study. The standard deviation of these measurements was 1.31% of the standard thickness. The error determined from 10 replicates of one experimental condition was 1.88%.

Conversion heat treatments were performed in a specially designed tube furnace with silica rails that allowed a silica setter plate with sample to be pushed into and out of a hot furnace. Sample temperatures were recorded by a thermocouple placed in a sleeve on the setter plate. The study of near-equilibrium film shrinkage behavior used a 5 °C/min ramp with a 1 h annealing at temperature followed by furnace cooling (approx. 5 °C/min above 500 °C). Heat treatments for other tests were modifications of heat treatment procedures that produced high *J<sub>c</sub>* films [11]. Fig. 1 illustrates the conversion heat treatment profiles. The initial ramp rate (to 500 °C) was 25 °C/min. The ramp rate between 500 and 760 °C was varied in the experiment from 5 °C/min to 25 °C/min. Samples were annealed at 760 °C for 2.25 h. All heat treatments were performed under 1 atm total, 100 ppm O<sub>2</sub>/balance N<sub>2</sub>, process gas flowing at 3 SLM through a 53 mm diameter quartz furnace tube. Three gas switches were made. The first switch occurred after 10 min at 760 °C and changed the moisture content of the process gas from the experimental

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