$YBa_2Cu_3O_{7-\delta}$ Formation by Processing of Laser-Ablated, Fluorine-Free Precursor Films

K. Kim, Y. Zhang, R. Feenstra, D. K. Christen, H. M. Christen, S. Cook, F. A. List, J. Tao, S. J. Pennycook, and Y. Zuev

***Abstract*—Epitaxial $YBa_2Cu_3O_{7-\delta}$ (YBCO) was formed by processing of laser-ablated, fluorine-free precursor films. The depositions were conducted at room temperature in low oxygen pressure on $LaAlO_3$ (LAO) single crystal substrates. Processing was done in the same deposition chamber by heating the precursor film to reaction temperatures of 750–850°C in a reducing gas ambient, and then raising the oxygen pressure to the conversion point. Typical processing times are a few minutes, corresponding to minimum YBCO growth rates of 1 nm/s. XRD analysis shows epitaxial growth and high crystallinity, although measured T_c values are somewhat suppressed at 88 K, with resulting critical current density, J_c of about 1 MA/cm^2 at 77 K, as determined by magnetic hysteresis. Properties indicate that the materials lack appropriate level of defects needed both for rapid oxygenation and flux pinning.**

***Index Terms*—Fluorine free process, high temperature superconductors (HTS), precursor films, pulsed laser deposition (PLD), YBCO processing.**

I. Introduction

THE c-axis oriented epitaxial $YBa_2Cu_3O_7$ films can be formed by various techniques. Coevaporation is one of the earliest proposed methods for $YBa_2Cu_3O_7$ film growth [1], [2]. Y, Cu, and BaF_2 from separate sources are coevaporated and an *ex situ* annealing in a wet oxygen ambient is performed. BaF_2 has been the preferred barium source in YBCO precursor films because barium metal can react in the air to form $BaCO_3$ [3]. $BaCO_3$ is known to be stable and difficult to decompose in the heat treatment process. The attractive aspect of BaF_2 process is that the precursor deposition and YBCO formation can be performed separately. This *ex situ* process made it possible to use different methods for growing precursor layers such as coevaporation, metal organic deposition [4] and sol gel processes [5]. BaF_2-containing precursor films are decomposed using water vapor resulting in the formation of gaseous HF [6], [7]. The reaction rate of BaF_2 decomposition and YBCO formation is determined by removal of HF by both gaseous convection and diffusion. The conversion to YBCO of fluorine free, environmentally stable PVD-deposited precursors may be conducted without the need of water vapor or the undesirable build-up and necessary removal of HF. Elimination of the latter could significantly simplify the conversion process, since high gas flow rates or low pressure processing [8] would be unnecessary. Using F-free precursors, large YBCO growth rates with excellent epitaxy and superconducting properties may be possible, based on the preliminary results of studies by Hammond *et al.* using electron beam co-evaporated YBCO precursors [9]. An additional potential benefit is expanded compatibility with various classes of lattice-matched buffer layers, which encompass many single-layer perovskite-like materials (to date, CeO_2 is the only buffer layer that has shown complete compatibility with the BaF_2 *ex situ* process).

Here we report the initial results on the formation of epitaxial YBCO on $LaAlO_3$ (LAO) single crystal substrates by converting fluorine free, laser ablated precursor films. In this study, the precursor film deposition and conversion processes were performed in the same chamber.

II. Experimental Procedure

The precursor films were formed by pulsed laser deposition (PLD) from a ceramic YBCO target onto single crystal LAO substrates at room temperature and in an oxygen ambient of 1.0×10^{-1} Torr. A KrF (248 nm) excimer laser was used as the ablation source at an energy density of 2 J/cm^2 and the repetition rate of 10 Hz. As-deposited precursor films with typical thickness of 0.2 μm were converted into crystallized $YBa_2Cu_3O_{7-\delta}$ structure by heat treatment in the same chamber, usually without breaking vacuum. A reducing gas mixture of $Ar/4\%H_2$ at a pressure of 1 Torr was admitted during heat up for processing. After the desired temperature was reached, oxygen was introduced rapidly as a processing gas. Guidance for the processing conditions of temperature and oxygen pressure were taken from the previous work of Hammond *et al.* [9], [10]. After a few minutes of processing, the temperature was decreased while maintaining the oxygen pressure. The resulting YBCO film was then annealed at 450°C in atmospheric oxygen ambient for 18 hours for further oxygenation.

X-ray diffraction $\theta - 2\theta$ scans were used to confirm the phase development in the films. Surface observation and the compositional analysis were conducted by SEM and energy dispersive x-ray spectroscopy (EDS). The superconducting transition temperature (T_c) and the critical current density (J_c) were measured with a SQUID magnetometer and a standard four-point

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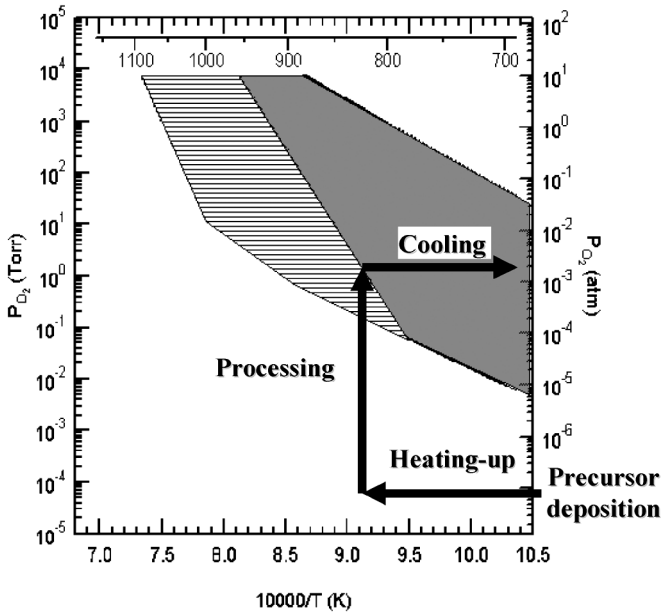

Fig. 1. The schematic procedure of in situ processing for laser-ablated, fluorine-free precursor film. This process consists of precursor deposition, heating up and conversion (processing).

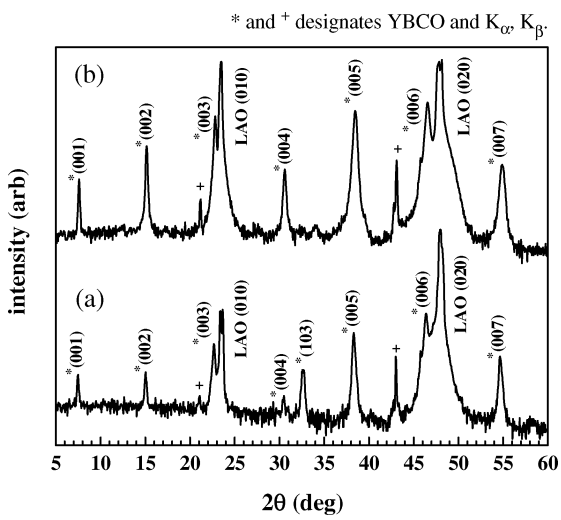

Fig. 2. X-ray diffraction $\theta - 2\theta$ scans of *in situ* processed $YBa_2Cu_3O_{7-\delta}$ films which were heated in (a) 3.0×10^{-1} Torr of oxygen and (b) 1 Torr of 4% Ar/H_2 mixture gas.

technique was used to evaluate the temperature-dependent resistivity. Atomic resolution Z-contrast imaging by scanning transmission electron microscope was used to analyze the YBCO crystal nanostructure.

III. Results and Discussion

The entire *in situ* processing procedure (without breaking vacuum) consists of three major steps: precursor deposition, heat up and conversion. Fig. 1 shows the schematic procedure of this processing related to the YBCO stability diagram. Heating the precursor film in the reducing ambient (1 Torr of $Ar/4\%H_2$) is an important parameter in order to obtain *c*-axis perpendicular YBCO. The x-ray diffraction $\theta - 2\theta$ scans in Fig. 2 show that heating the precursor film in an oxygen ambient produces a polycrystalline YBCO component. The as-deposited precursor

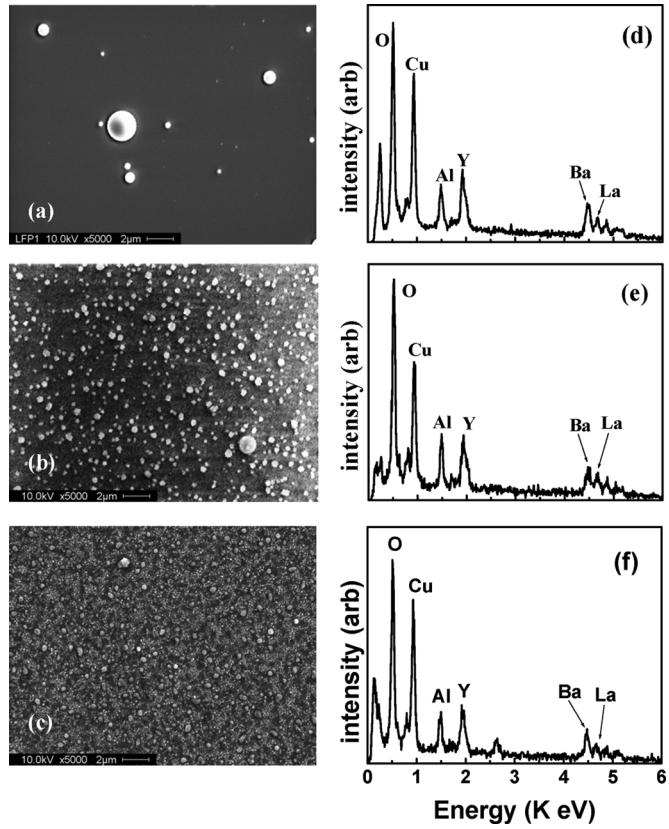

Fig. 3. The surface SEM pictures of (a) as deposited precursor film, (b) as heated precursor film in 4% Ar/H_2 gas and (c) processed YBCO film. The EDS graphs of (d) as deposited precursor film, (e) as heated precursor film and (f) processed YBCO film. La and Al peaks come from the substrate.

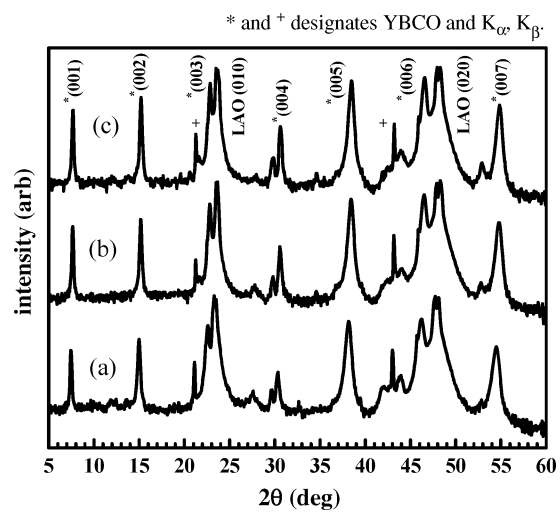

Fig. 4. The x-ray diffraction $\theta - 2\theta$ scans of *in situ* processed $YBa_2Cu_3O_{7-\delta}$ films at different processing temperatures of (a) 780°C, (b) 820°C and (c) 850°C.

film on LAO showed a smooth surface with some particulates as shown in Fig. 3(a). Although the as heated precursor film and *in situ* processed YBCO film showed different surface morphology in Figs. 3(b) and 3(c), the composition and the Y : Ba : Cu ratios from EDS analysis remained same after processing as indicated in Figs. 3(d), 3(e), and 3(f)

Fig. 4 is the x-ray diffraction $\theta - 2\theta$ scans of $YBa_2Cu_3O_{7-\delta}$ films processed *in situ* at the different processing temperatures

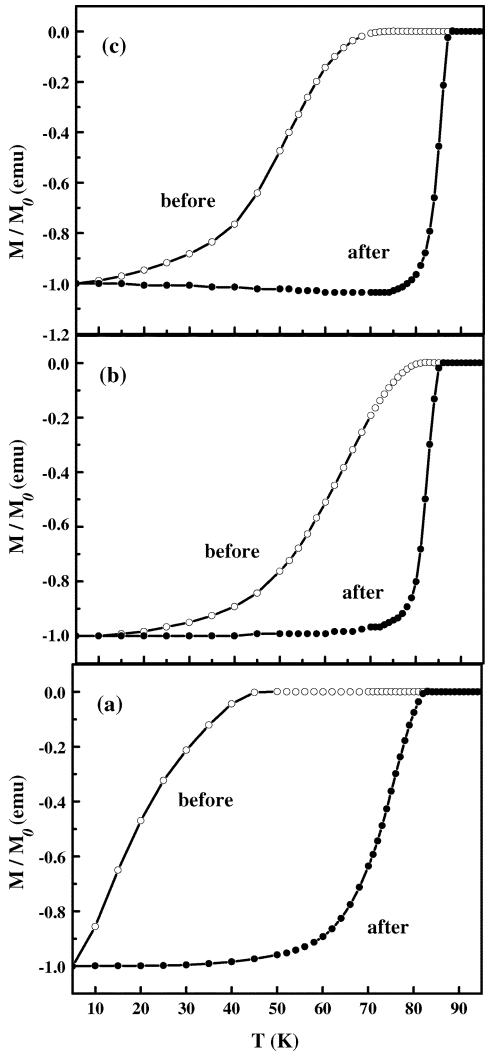

Fig. 5. The low-field magnetization versus temperature graphs of *in situ* processed $YBa_2Cu_3O_{7-\delta}$ films. Processing temperatures were (a) 780°C, (b) 820°C and (c) 850°C. Samples are compared before and after oxygenation at 450°C in 1 atm of oxygen for 18 hours.

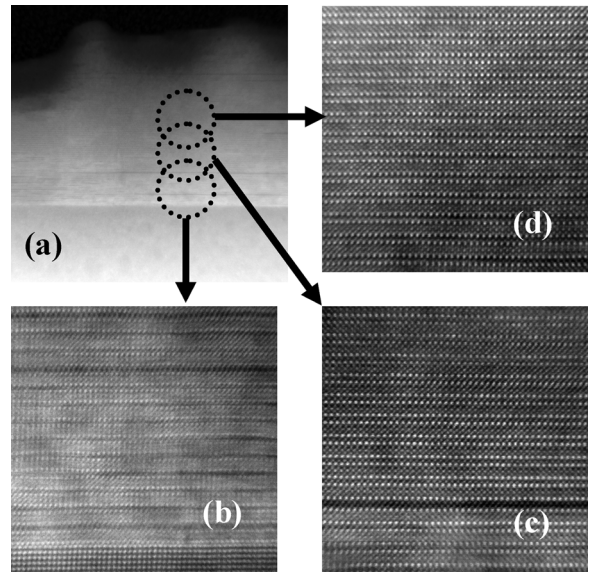

Fig. 6. The Z-contrast STEM images of (a) low resolution cross-section, (b) interface between LAO substrate and YBCO, (c) middle part of the YBCO film and (d) upper part of the YBCO film.

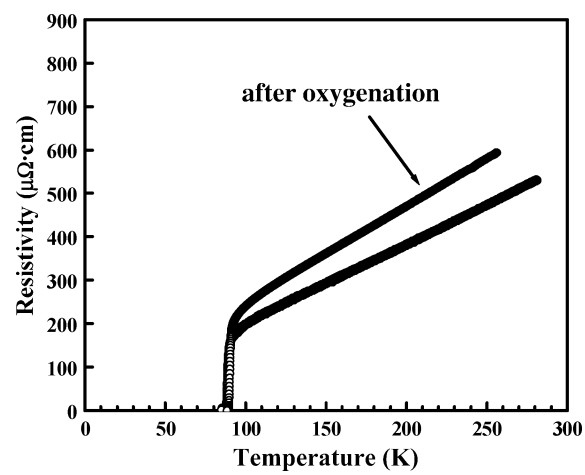

Fig. 7. The resistivity versus temperature graph of a YBCO film on SrTiO3 substrate processed *in situ* at 820°C, before and after oxygenation at 450°C in 1 atm of oxygen for 24 hours.

of 780°C, 820°C and 850°C. No significant phase differences were found in these x-ray patterns. The superconducting transition temperatures of these YBCO films measured magnetically at 4 Oe are indicated in Fig. 5. The offset temperatures are below 80 K in each case, and sharp transitions cannot be observed. However, long-term oxygen annealing at 450°C in 1 atm of oxygen for 18 hours improved the T_c values.

In order to understand the need for the long oxygenation times, the YBCO nanostructure was observed by Z-contrast STEM. Fig. 6(a) is a low resolution ZSTEM image showing both the LAO substrate and the processed YBCO film. Figs. 6(b), 6(c), and 6(d) are images taken near the interface between the LAO substrate and YBCO film, the middle part of YBCO film and the upper part of YBCO film, respectively. The images taken at different scales show that the F-free in situ processed YBCO film is nearly defect free. Of the few observable defects, most are planar intergrowths in the ~20 nm layer near the YBCO-substrate interface. There is improved perfection away from the interface, and virtually no threading defects through the film thickness can be observed. The lack of visible nanoscale defects is consistent with the difficulty in oxygen uptake. Oxygen tracer diffusion studies in single crystalline YBCO have shown that the diffusion coefficient of oxygen in c-direction is about 10^{-6} of that in the a or b direction [11]. As a result, lack of c-axis oriented defects render it difficult to achieve complete oxygen uptake. Fig. 7 is the resistivity versus temperature graph of a processed YBCO film on $SrTiO_3$ substrate, before and after a long-term oxygen anneal. In this case, the resistivity was not improved by the low-temperature soak. Fig. 8 shows the magnetically-determined J_c values at 5 K and 77 K. The F-free processed YBCO film grown on LAO substrate showed J_c value of 1.06 MA/cm^2 at 77 K which is lower than an *ex situ* YBCO from comparable PVD BaF_2-based precursors. The J_c dependence on the magnetic

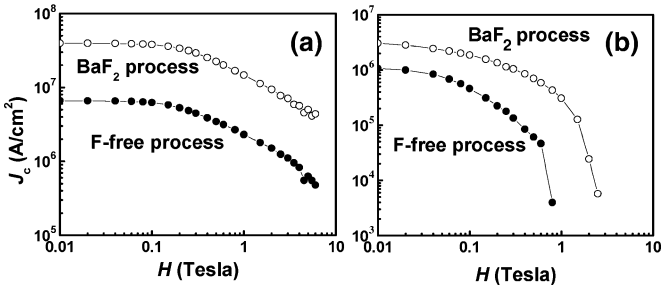

Fig. 8. The current density versus magnetic field graphs of *in situ* processed YBCO precursors on $LaAlO_3$ substrate compared with YBCO processed from a BaF_2 precursor at (a) 5 K and (b) 77 K.

field shows relatively weak flux pinning which can also be explained by the lack of defects inside the YBCO film.

IV. Conclusion

Epitaxial thin films of YBCO have been synthesized from F-free, laser ablated precursors. Processing for the best materials involves raising the oxygen pressure after heating in a reducing ambient such as 4% Ar/H_2 mixture gas. The superconducting transition temperature was measured to be 88 K, with resulting critical current density of about 1 MA/cm^2 at 77 K, as determined by magnetic hysteresis. Properties indicate that materials lack an appropriate level of defects needed both for oxygenation and flux pinning.

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