$YBa_2Cu_3O_{7-\delta}$ FILMS THROUGH A FLUORINE FREE TMAP MOD APPROACH

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ABSTRACT

$YBa_2Cu_3O_{7-\delta}$ (YBCO) films were fabricated via a fluorine free metal trimethylacetate (TMA) proponic (P) acid and Amine based sol-gel route (TMAP) and spin-coat deposited on single crystal (001) $LaAlO_3$ (LAO) and (001) $SrTiO_3$ (STO) with a focus on optimizing the processing parameters in the non-fluorine chemical solution deposition (CSD). Trimethylacetate salts of copper and yttrium and barium-hydroxide were used as the precursors, which were dissolved in proponic acid and Amine based solvents. A 180 ppm oxygen partial pressure and water vapor atmosphere were employed for the pyrolysis at 745°C for one hour. A critical transition temperature (T_{c0}) of 90K and a critical transport current density (J_c) of 0.5 MA/cm^2 (77 K and self-field) were demonstrated for the YBCO film on (001) oriented LAO substrates with a thickness of 300 nm. A FWHM of 0.6° for the (005) omega scan shows good out-of-plane texture. In (113) phi scans, the peaks are 90° apart with a FWHM of 1.4° showing good in-plane textures. A good in-plane texture is also shown in (113) and (115) pole figures. The TMAP approach is promising for high current density and high film quality.

INTRODUCTION

Chemical solution deposition (CSD) is one of the deposition techniques used to fabricate YBCO films. CSD has some advantages over vapor deposition of YBCO such as precise control of composition, high speed, and low-cost. Metal Organic Deposition (MOD), one of the popular CSD methods, involves the coating of an organic precursor solution on a substrate followed by thermal decomposition to form the final desired compound. Epitaxial nucleation and growth can occur when the process is carried out on lattice matched single crystal substrates. Trifluoroacetate (TFA) MOD is well established as a promising

method for the fabrication of high J_c (over 1 MA/cm^2) YBCO films[1,2] and has been applied on biaxially textured metal substrates like RABiTS[3,4]. The interest in fluorine-containing precursors for YBCO arises because it is believed that non-fluorine precursors might result in the formation of stable $BaCO_3$ at the grain boundaries[5]. The use of TFA salts appears to avoid the formation of $BaCO_3$ because the stability of barium fluoride is greater than that of barium carbonate and fluorine can be removed during the high temperature anneal (>700°C) in a humid, low oxygen partial pressure environment[2]. Nonetheless several factors maintain interest in a fluorine-free precursor MOD approach. The most important being that removal of fluorine at high temperatures is a non-trivial process. There appear to be many issues related to fluid-flow and complicated reactor designs may be required for scale-up. In this work, we report on the fabrication of high quality YBCO films using a fluorine-free precursor. The transport critical current density of these films is over 0.5 MA/cm^2 at 77 K and self-field.

EXPERIMENTAL

Films were prepared by the following procedure[6,7]: yttrium trimethylacetate, barium hydroxide, and copper trimethylacetate were dissolved into proponic acid and amine solvents in a controlled stoichiometry (Y:Ba:Cu=1:2:3) to form a dark green solution with a total ionic concentration of 0.5-0.8 M. After filtration, this solution was applied onto the substrates in a spin-coater at speed of 2000-5000RPM. A 200-250°C baking step was used between multi-coatings on a hot plate to make thicker films. Burn out was carried out in the quartz tube furnace at 400°C for 10 hours in a humid pure oxygen atmosphere. These intermediate films were then subject to a high temperature anneal in which they were heated to 700 - 860°C at 10-40°C/min and held in a low oxygen partial pressure for 1-2hrs. Following the hold, the furnace atmosphere was switched to dry, and later to dynamic dry oxygen. All films were slow-cooled in oxygen to 500°C where they were held for 0.5-3hrs and furnace-cooled to room temperature in flowing oxygen. Humid gas was introduced into the furnace in the burned-out stage and prior turning on pure oxygen in the annealing stage. J_c was measured in the usual four-point transport method at 77 K and zero field. In addition, for selected samples, texture was analyzed by x-ray diffraction, surface morphology was characterized by scanning electron microscopy (SEM) and TGA was used for the thermal decomposition analysis.

RESULT AND DISCUSSION:

Fig. 1. shows Thermal Gravimetric Analysis (TGA) results for the copper trimethylacetate and yttrium trimethylacetate precursors. For the copper trimethylacetate precursor, the weight reduces quickly when the temperature increases beyond 200°C, and then become constant after 250°C, which

demonstrates the full decomposition of copper trimethylacetate at that temperature. For yttrium trimethylacetate precursor, the decomposition occurs over a wider range and is finished at about 520°C. Weight losses are structure-related thermal processes and reflect the binding energies. Different atmospheres, for example, air and pure oxygen, have minor effects on the shapes and temperatures of TGA curves both for copper trimethylacetate and yttrium trimethylacetate precursor.

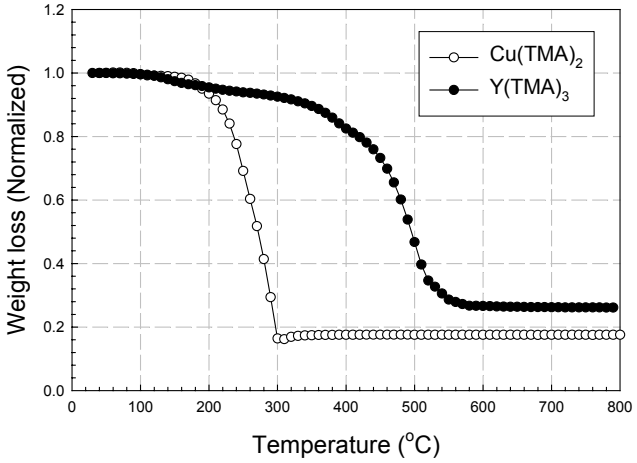

Fig. 1. Weight loss in TGA analysis for copper trimethylacetate and yttrium trimethylacetate precursors, atmosphere: N_2 with Po_2=100-200ppm, ramp: 10°C/min.

CuO is easily evaporated at elevated temperature in dry atmosphere. The decomposition temperature for copper trimethylacetate (250°C) is lower than those of yttrium trimethylacetate (520°C) and barium hydroxide[8] (490°C). In considering CuO formation during the decomposition of copper trimethylacetate, keeping the baking temperature below 250°C is reasonable to prevent the loss of CuO between multi-coatings. But when the baking temperature is less than 150°C, later coatings dissolve away former ones easily. So normally 200-250°C for 3-5 minutes was used for the baking process.

In the burn out stage, several temperatures (310-600°C) were selected to control reactions of the components in precursor decomposition. 400°C was used as an optimized temperature for the burn out stage because rough surface morphologies of YBCO film were observed routinely on samples burned out below 400°C (for example, 310°C) and above 400°C (for example, 500°C and 600°C). For this research, four temperatures 725°C, 745°C, 780°C, and 820°C

were used for high temperature annealing. Fig. 2 shows the θ-2θ scans of YBCO films annealed at 745°C and 820°C respectively.

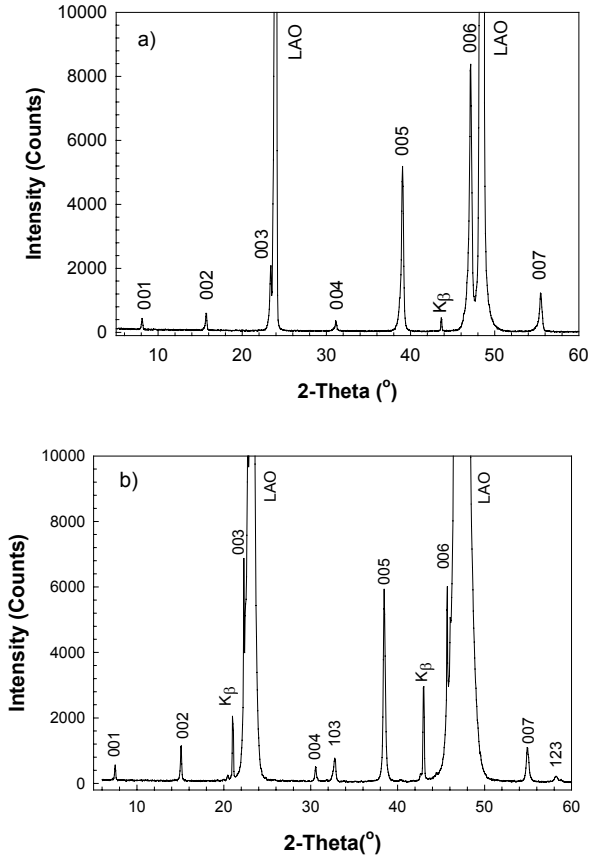

Fig. 2. θ-2θ scans of YBCO thin film on (001) LAO single crystal substrates burned out at 400°C in wet O_2 and high temperatures annealed in low oxygen partial pressure (Po_2=180ppm) for 50min wet and 10min dry at different temperatures: (a) 745°C, (b) 820°C

Only substrate peaks can be detected for the films burned out at temperatures below 400°C, indicating that the film is amorphous. YBCO (00*l*) peaks can be identified for samples annealed at 700°C and are stronger after annealing at 725°C for one hour. The (103) peak is seen when the temperature is beyond 780°C, especially for the sample annealed at 820°C as shown in Fig. 2 b). All (00*l*) YBCO peaks are shown in Fig. 2 a). The absence of other YBCO peaks confirms that the YBCO has good out-of-plane texture. The values of FWHM (Full Width at Half Maximum) of the (005) rocking curves are small and nearly constant (0.6°) for the samples annealed at 725°C, 745°C, and 780°C, demonstrating high quality *c*-oriented texture of these YBCO films. In the (113)

phi-scan, Fig. 3, peaks are 90° apart with a FWHM of 1.4° showing good in-plane texture for a sample annealed at 745°C for one hour. This sample also had the highest YBCO intensities both for ω-scans and ϕ-scans.

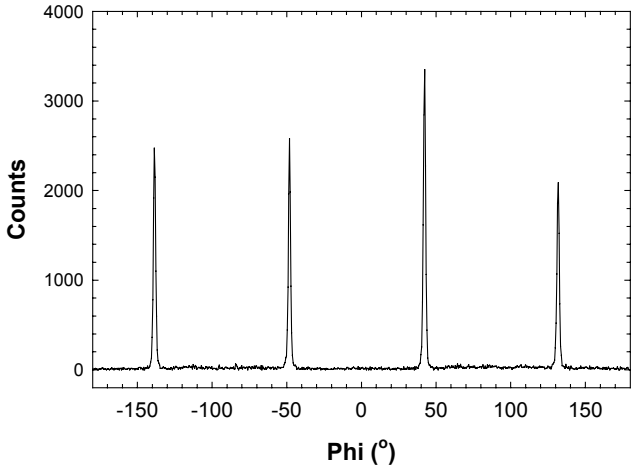

Fig. 3 The 113 ϕ-scan of YBCO films on LAO (001) substrate burned out at 400°C and annealed at 745°C for one hour in humid Ar/O_2 atmosphere with Po_2=180ppm

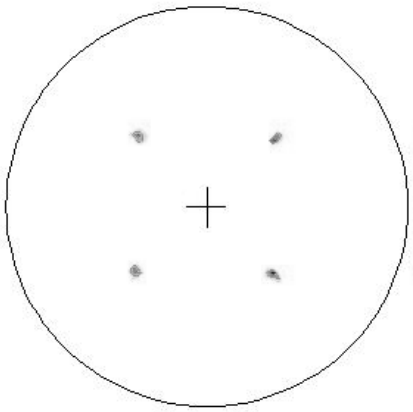

Fig. 4 The YBCO (115) pole figure of 400°C burned out film and annealed at 745°C/1hr in humid Ar/O_2 atmosphere with Po_2=180ppm

Pole figures were obtained to get a more complete examination of the degree of epitaxy. For 745°C annealed sample, only four small poles located on the correct positions on the pole figure plot, Fig. 4, confirms that the YBCO phase grows epitaxially on the LAO substrate. The T_c measurement shows a sharp

transition with zero resistance at 90 K for the sample annealed at 745°C for one hour, but broader transitions were detected for samples annealed at 725°C and 780°C. A semiconducting transition behavior was observed for the 820°C annealed sample. The transport critical current density (J_c) of 0.5 MA/cm^2 was obtained at 77 K in self-field for the 745°C annealed sample. Very low critical currents were observed for YBCO films annealed at 725°C and 780°C. For the film annealed at 820°C for one hour, the critical current was zero.

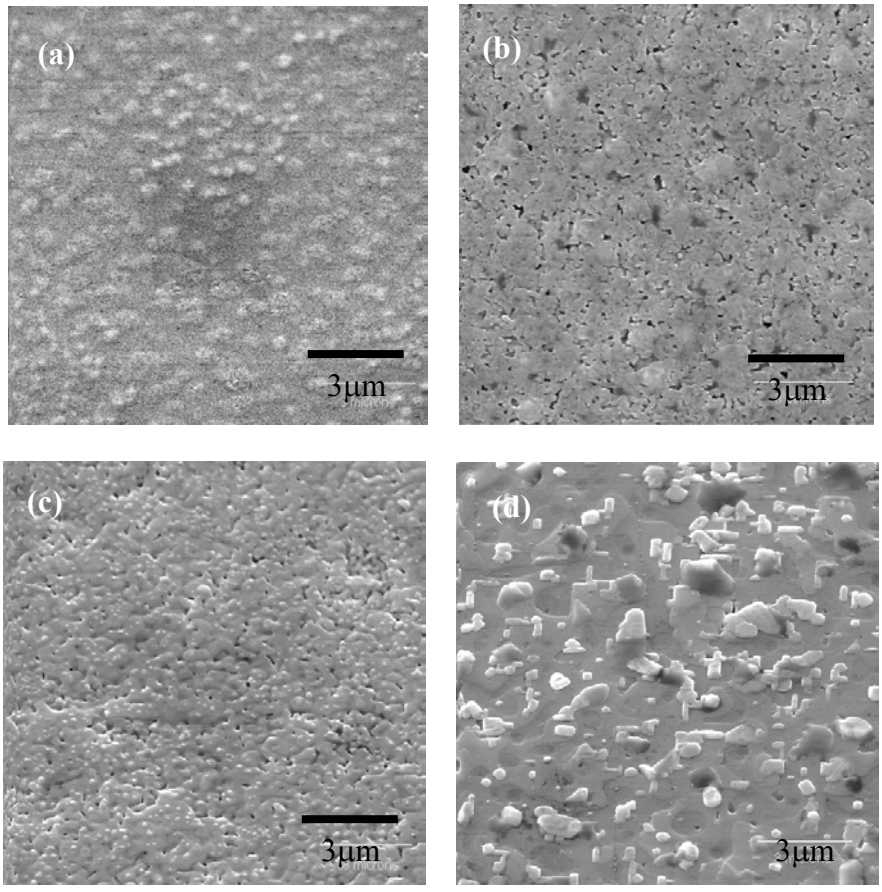

Fig. 5. SEM morphologies of YBCO thin films heat-treated at different temperatures. (a) 600°C burn out in wet oxygen; (b), (c), and (d): 400°C burn out in wet oxygen and annealed at 725°C/1hr, 745°C/1hr, and 820°C/1hr respectively in Po_2=180ppm wet atmosphere.

For samples annealed at 600C, evidence of crystallization is obtained. Crystallized regions in the form of dots can be seen on the sample surface as shown in Fig. 5a. No composition difference can be identified by EDS (Energy Dissipation Spectra) on dots and other areas. Associated with the decomposition

of the copper trimethylacetate and yttrium trimethylacetate precursors in the TGA analysis (Fig. 1), it is believed that these dots are the decomposition products formed initially in the green films. As the decomposition of the copper trimethylacetate occurs at relative low temperature, and the resistivity (calculated from resistance of quenched sample during 600°C burn out) can go as low as 0.1-0.01 Ω-cm, correlating these dots with CuO is reasonable. The distribution density of these dots is comparable with that of grains; thus they might be the places for the further reactions and/or nucleations of YBCO phase. The surface morphology of the 725°C and 745°C annealed samples is relatively smooth, although some pores decorate the surface. From the SEM micrograph Fig. 5 (b), it is appears that the microstructure of the 725°C annealed sample is not fully developed. This is also supported by XRD data and the results of electrical property measurements. The lack of full conversion to YBCO is the reason for the low J_c and relatively broad transition temperature in the superconducting transition. Irregularly shaped surface segregates are observed commonly on samples annealed higher than 820°C as shown in Fig. 5 (d). The rough surface is obviously related to the over reaction among the components and with the environment such as humid gas, or to the decomposition of YBCO phase as reported in the literature[9]. With the rough surface coupled with texture changes shown in XRD data, no good electrical properties can be expected on samples annealed at temperature beyond 820°C.

The morphology of the 745°C annealed sample is similar to that reported by R. Feenstra *et al*[9]. in e-beam derived YBCO films with post annealing. Enhanced growth of plate-like grains, smooth surface, absence of large pores and second phase particles, and the absence of *a*-axis oriented grains indicate the potential for high critical current density.

SUMMARY

A fluorine-free Metal Organic Deposition (MOD) method was employed for the fabrication of $YBa_2Cu_3O_{7-\delta}$ films. A T_c of 90 K and a transport critical current density (J_c) of 0.5 MA/cm^2 (77 K and self-field) were demonstrated for the YBCO film on (001) oriented LAO substrate annealed at 745°C for one hour in humid furnace gas with oxygen partial pressure of 180ppm. There is no evidence that $BaCO_3$ is formed as an intermediate compound during decomposition of the precursors in well-prepared samples. SEM morphology reveals that feature development on top of the film occurs much earlier than crystallization takes place (as revealed by XRD data). Annealing temperature is critical for the YBCO phase development in low oxygen partial pressure and humid furnace gas. Undeveloped phases and poor texture at relatively low annealing temperature are the reasons for the low current densities. The YBCO phase seems to decompose at

relatively high annealing temperatures (820°C) resulting in a rough surface and a semiconductor behavior.

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