



Optimization of Non-Fluorine Sol-Gel Derived YBCO Thin Films

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Abstract. Sol-gel deposition of thin film $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) is widely seen as the most cost effective means to manufacture long length HTS wires (A.P. Malozemoff, D.T. Verebelyi, S. Fleshler, D. Aized, and D. Yu, "HTS Wire: Status and Prospects," *Physica C*, **386**, 424 (2003)). We present a sol-gel technique for YBCO deposition using low cost starting materials and forming only benign by-products during processing. Optimization has concentrated on producing the correct stoichiometry in the final films. RBS measurements show that copper diffuses into the substrate due to its high mobility at the temperatures required to form the YBCO phase. Therefore a starting stoichiometry of 1:2:3 can produce a film highly copper deficient. In order to compensate for this we have made films with different excesses of copper in the precursor solution. The surface morphologies of these films have been examined by SEM and AFM, and the stoichiometry and cation depth profiles characterized by ion beam analysis. The effect of the varying copper stoichiometry is correlated with the superconducting properties and the surface morphology for films on lanthanum aluminate (LAO) and magnesium oxide (MgO) substrates. The residual carbon concentration in the films is measured by nuclear reaction analysis.

Keywords: YBCO films, stoichiometry, sol-gel deposition

1. Introduction

Sol-gel methods allow high quality, large area films to be produced rapidly and inexpensively. The trifluoroacetate (TFA) precursor produces high quality films [2], however the corrosive toxic gas HF is produced as a by-product which may present problems in large scale manufacture. Alternatively, non-fluorine based precursors can produce high quality films as improvements in sol-gel techniques now allow atomic level mixing of cations [3]. We have developed a non-fluorine precursor that is inexpensive, environmentally friendly, rapidly synthesized and stable at high concentrations [4, 5]. The growth of films on MgO is of interest as textured MgO can be produced rapidly by ion beam assisted deposition (IBAD) for long length tapes. The growth of YBCO directly on MgO would obviate the need for extra buffer layers.

The precursor is spin-coated onto lattice-matched substrates, then decomposed to YBCO. RBS measurements show that during the high phase forming temperature copper diffuses into the substrate. Therefore a precursor stoichiometry of 1:2:3 produces a copper deficient final film. However, one advantage of sol-gel techniques is that a high degree of stoichiometric control is afforded. A series of precursors with different copper stoichiometry was prepared to produce films with optimum composition. The effect of the stoichiometry on the surface morphology, resistivity, copper diffusion profile, cation disorder and the carbon contents of these films was examined for this optimization.

2. Experimental

As described in more detail elsewhere [4, 5] YBCO precursor solutions were prepared by reacting standardized aqueous yttrium, barium and copper acetate solutions with malic acid and were then stabilized in a glycerol-water solvent mix (all reagents Aldrich). A

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series of precursors of Y:2Ba:zCu, with $z = 3\text{--}4.2$ were prepared. The solutions were spin-coated onto thermally pretreated lattice-matched (100) LAO and (100) MgO single crystal substrates.

The water is carefully removed from the film, which then undergoes a series of pre-firing thermal treatments. To form the YBCO phase the film is reacted for 2 hours at 850°C and 3×10^{-3} atm O_2 . The film is oxygen loaded during the cool down in the furnace.

Films were made on LAO substrates with precursor excesses of copper $z = 3\text{--}3.6$, and on MgO substrates with $z = 3.2\text{--}4.2$. Higher z was used for MgO than LAO as it was expected that more copper would diffuse into the substrate due to the lower density of MgO compared with LAO ($3.58 \text{ g}\cdot\text{cm}^{-3}$ cf. $6.52 \text{ g}\cdot\text{cm}^{-3}$) and higher fraction of interstitial space (0.373 cf. 0.261).

Characterization of the films included confirmation by X-ray diffraction that c -axis oriented YBCO films were produced (results not shown). The temperature dependence of the electrical resistivity was measured using a standard four terminal technique. Microstructure was observed by SEM (LEO440) and AFM (PicoSPM). Raman microscopy, used as a probe of cation disorder was performed with a Jobin Yvon Horiba HR800.

Ion beam analytical techniques including Rutherford Backscattering Spectroscopy (RBS) were used to determine the thickness and stoichiometry of the films and Nuclear Reaction Analysis (NRA) to measure carbon contents, which have a detrimental effect on the film quality. A $2.5 \text{ MeV } ^4\text{He}^+$ beam obtained from a 3 MV accelerator was used for these measurements.

3. Results and Discussion

The reacted films vary in microstructure with z . The surface roughness of the films on LAO, shown in Fig. 1, was estimated by applying line profiles to SEM images. These results agree with the RMS roughness measured by AFM, not displayed.

The smoothest films had $z = 3.2$ on LAO, and $z = 3.6$ on MgO, although no trend in roughness vs. stoichiometry was observed on MgO. AFM images, shown in Fig. 2 illustrate the difference in feature size of the smoothest films on the two different substrates. LAO may have a higher density of nucleation sites due to the high density of twin planes in the material. This would then give rise to the smaller YBCO feature size.

The resistivity temperature dependence is substrate dependant as shown in Fig. 3. The films with lowest

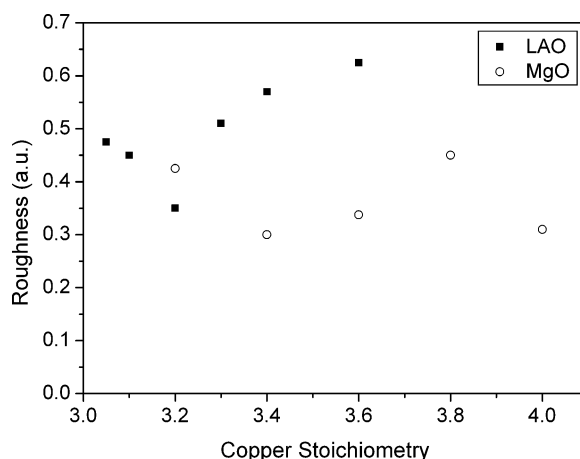


Fig. 1. Roughness vs. stoichiometry for films produced on LAO and MgO.

normal resistivity occurred for $z = 3.1$ on LAO and $z = 4$ on MgO. Despite the higher resistivity, the films on LAO have consistently higher superconducting transition temperatures with sharper transitions, and the intercept of normal state resistivity is closer to the origin. These resistivity values compare favorably with literature values for YBCO films.

Raman spectroscopy gives a measure of the cation disorder in YBCO films [6]. The peak at 340 cm^{-1} shows the in-plane texture of YBCO grains and is optimized with strong texture; the peak at 500 cm^{-1} , an O(4) mode, is a measure of how close the oxygen stoichiometry is to 7, and is weak for $\delta \cong 0$; and the presence of a peak at 575 cm^{-1} (CD), a defect activated breaking of symmetry, signifies cation disorder.

No CD peaks were seen in the films on LAO, and the optimal $340:500 \text{ cm}^{-1}$ ratios occurred for $z = 3.1$ and 3.2 as shown in Fig. 4. On MgO the CD peak decreased with increasing z , showing the cation disorder in the film is reduced with increasing copper stoichiometry, in agreement with the resistivity results. The low copper stoichiometry ($z = 3.2$) film had a relatively small 340 cm^{-1} peak, showing poor texture. Only small amounts of variability in the ratio of the $340:500 \text{ cm}^{-1}$ peak heights were seen in the other films on MgO. Overall the results demonstrate the better crystalline quality of the films on LAO.

The RBS spectra in Fig. 5 show the yttrium, barium and copper depth profiles. The films were deliberately made very thin to facilitate this measurement. The copper profile extends past the depth of the yttrium and

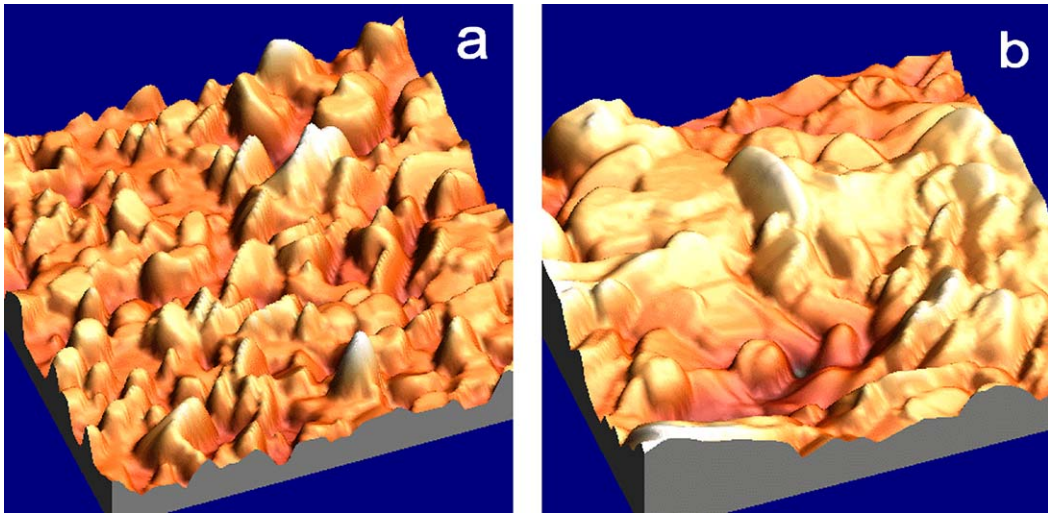


Fig. 2. 3D AFM image of the smoothest film on (a) LAO, with $z = 3.2$, and (b) MgO, with $z = 3.6$. The area shown is $10 \mu\text{m} \times 10 \mu\text{m}$.

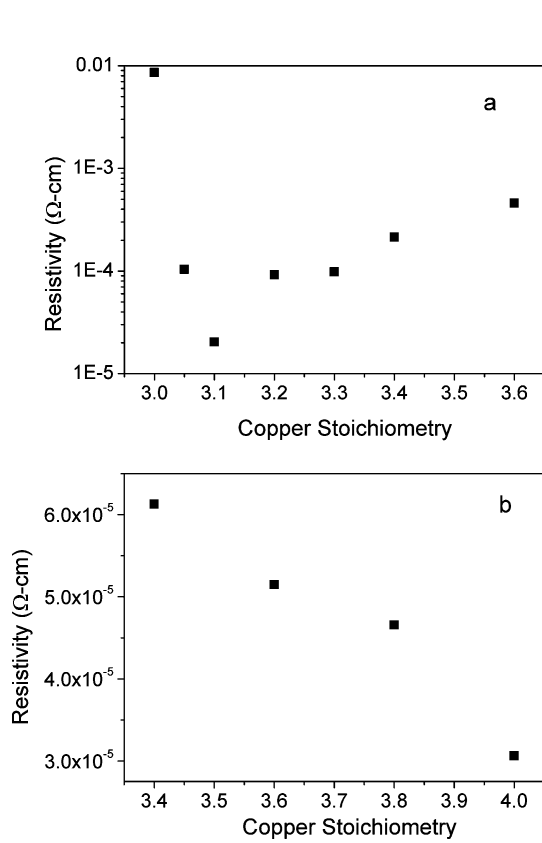


Fig. 3. The residual resistivity of YBCO films with changing copper stoichiometry on (a) LAO and (b) MgO.

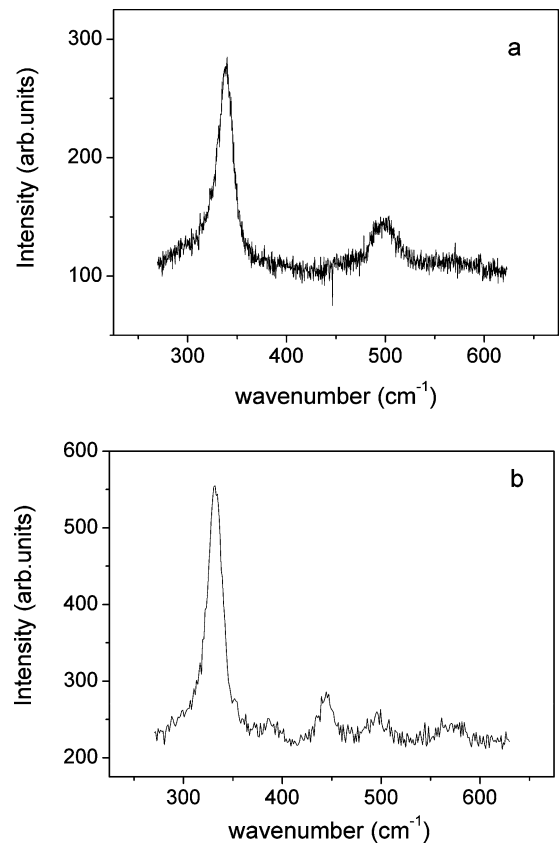


Fig. 4. Raman spectra from optimal films on (a) LAO, with $z = 3.2$ and (b) MgO, with $z = 3.4$.

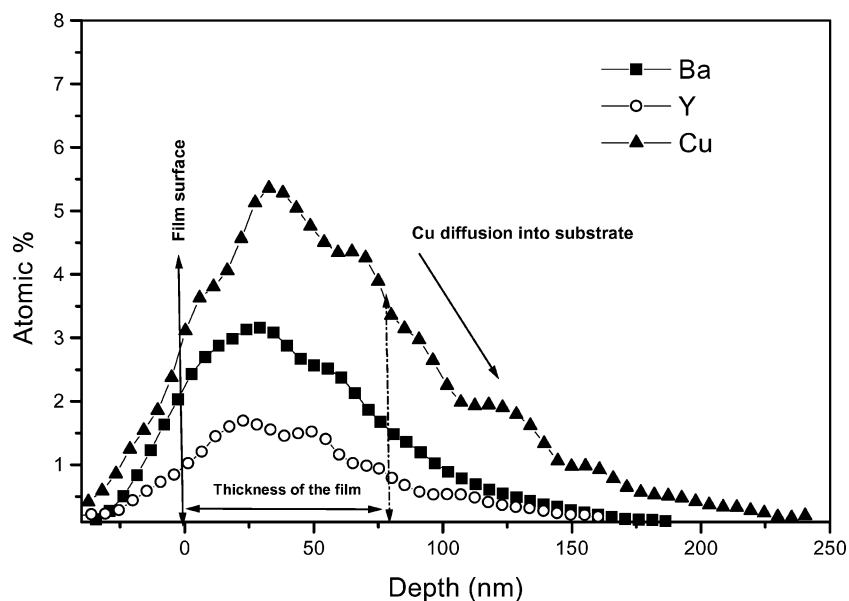


Fig. 5. RBS depth profile of Y, Ba and Cu from a YBCO film on an MgO substrate.

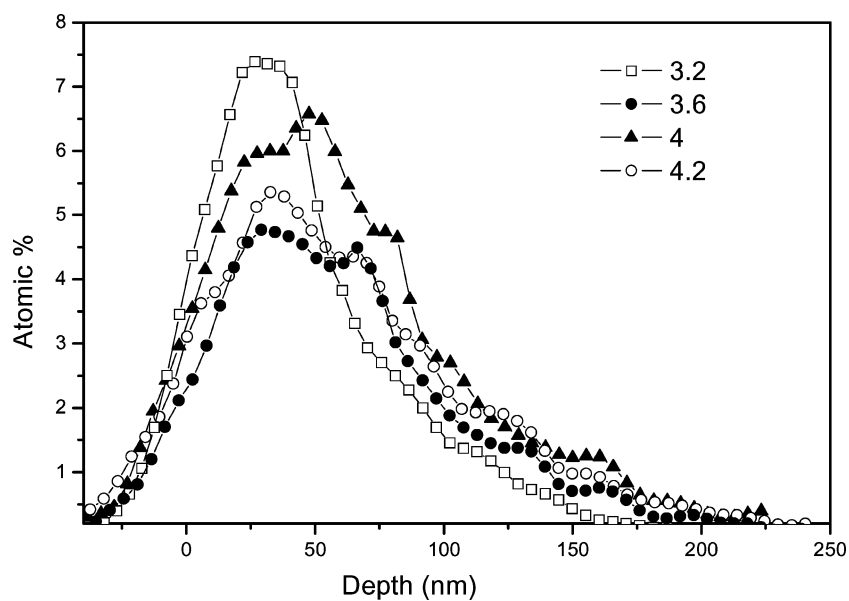


Fig. 6. Diffusion profile of copper in fully processed YBCO films on MgO substrates for different z .

barium profiles, and has an additional peak in this region, indicating the diffusion of copper into the substrate. This produced copper deficient films when a precursor stoichiometry of $z = 3$ was used.

RBS was used to determine the film stoichiometries after conversion to YBCO. Most of the films showed

close to ideal stoichiometry, with little variation given the difference in the precursor compositions. However, precursors volatilization may occur at high temperature [7], thus diffusion may not account for the total loss of copper. Our results indicate that excess copper encourages further diffusion into the substrate

or volatilization. For both LAO and MgO substrates the highest copper concentrations in the precursor have lower copper concentrations than expected in the final films.

Figure 6 shows the copper profile on MgO substrates for $z = 3-4.2$. The peak heights vary with film thickness, however the penetration depth of copper, defined by the depth at which the concentration drops to zero, increases with z . Deviations in uniformity from the Gaussian curve indicate the degree of surface roughness in the film, which increases with z . This is due to the formation of a copper rich layer in the substrate.

Carbon is an unwanted impurity and its elimination during processing is necessary to optimize film quality. The residual carbon concentration in our films was measured by nuclear reaction analysis. The average concentration remaining in the films was of 0.5 atomic %, with no variation observed with films thickness from 100–750 nm. The carbon content was independent of the substrate or the stoichiometry.

4. Conclusions

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films were made by spin-coating an inexpensive, non-toxic, metal-organic precursor onto LAO and MgO substrates. This method has good stoichiometric control, important for optimizing the precursor as RBS measurements show the loss of copper stoichiometry by diffusion into the substrate at the phase-forming temperature.

To produce fired films with the desired 1:2:3 stoichiometry, a series of films with excess copper in the precursor was produced and analyzed for optimal smoothness, resistivity and cation disorder. On LAO,

the stoichiometry that produced the smoothest, best film was around $z = 3.1$ to 3.2, a copper excess of approximately 5% above the stoichiometric amount. On MgO the results were less conclusive, though clearly the residual resistivity was improved by the addition of excess copper. The organic component of the films was broken down cleanly, leaving approximately 0.5 at.% carbon.

Future work will focus on reducing the reaction temperature to minimize diffusion and volatilization. Substrate preparation will be optimized to improve nucleation on MgO. Control of the final film stoichiometry will simplify the optimization of the critical current.

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