Chemical synthesis of spun-on thick films of oxide superconductors

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Abstract
Films of YBa$_2$Cu$_3$O$_{7-x}$ were deposited by a metal organic decomposition onto single crystals of MgO and Al$_2$O$_3$, polycrystalline Ag, and stabilized ZrO$_2$ substrates by spin coating. The precursor solution of metal acetates dissolved in citric acid and ethylene glycol were found to produce films which decomposed without surface damage. The surfaces of the samples, examined by a profilometer, were found to be continuous, smooth and had good adherence to all of the substrates. The films showed a broad superconducting transition temperature starting at 89 K.

1. Introduction
One of the most promising research areas in high-$T_c$ superconductivity is in thin and thick films and coatings. There are immediate uses for these materials as thick coatings for magnetic shielding applications, as thin films for electronic applications in superconducting quantum interference devices (SQUIDs) [1] and infrared detectors [2]. Thin films of the superconducting oxide show superior properties when deposited by laser ablation [3], molecular beam epitaxy [4], sputtering [5], and electron beam evaporation [6], but these methods are too slow and costly to fabricate films of substantial thickness.

During the past twenty years it has become well known that oxide films with chemically pure, fine and uniform grain sizes can be formulated via solution chemical decomposition techniques. With the application of solution techniques, it is possible to form films by dipping, spinning or spraying the liquid and then decomposing the homogeneous, atomically mixed fluid or gel into a smooth film of uniform thickness. Novel chemical synthesis techniques have been used in tandem with these deposition methods to produce films of the superconducting oxide using processing routes such as dipping-pyrolysis [7], spin-on coatings [8] and spray drying [9]. These coatings are generally amorphous and crystallize at elevated temperatures as water and volatile organic solvents are evaporated. Chemical routes are simple to use, cheap, easily controlled and require no expensive vacuum equipment.

We have undertaken a study to produce films of the superconducting oxide by spin-coating organic solutions of metal acetates dissolved in citric acid and ethylene glycol to examine the cohesiveness and continuity of the films.

2. Experimental techniques
Metal acetates* [M$^+$(OOCCH$_3$)$_2$, where M = Y, Ba or Cu] were mixed in the stoichiometric molar ratio of Y:Ba:Cu = 1:2:3 and dissolved in deionized water with a total metal cation molarity of 3 M. One mole of citric acid to two moles of ethylene glycol were added to polymerize the solution according to the reaction:

\[
\text{citric acid} \quad \text{ethylene glycol} \quad \begin{array}{c}
\text{OH} \quad \text{O} \\
\text{H} \quad \text{C} \quad \text{O} \\
\text{O} \quad \text{R} \quad \text{OH} \\
\text{C} \quad \text{OH} \quad \text{R} \quad \text{O}
\end{array}
\]

The molar ratio of citric acid:total metal cations was kept at 2.3:1, which minimized the amount of excess carbon added to the solution [10]. The solution was allowed to stir under heat with a pH = 2.5. We experienced no precipitation problems with this acidic solution. The solutions were analyzed by thermogravimetric analysis (TGA) and by differential thermal analysis (DTA).

The solutions were then deposited onto various substrates by a spin-coating method. The substrates used were single crystals of MgO and Al$_2$O$_3$ and polycrystalline silver and yttria stabilized zirconia. The substrates had an average surface area of 0.7 x 0.7 cm$^2$ and were cleaned in RBS-35† in a heated ultrasonic bath, rinsed with acetone and dried. Each substrate was put on the spin coater which rotated at a speed $\approx 500$ r.p.m.

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The solution was applied by dropping $\approx 15 \mu l$ on the spinning substrate which was spun for 1 min to ensure even distribution. The substrate was immediately inserted into an oven at 500 °C and allowed to sit for 1.5 min to volatilize the low vapor pressure species. The coating turned a dark brown but maintained a smooth, uniform appearance. The sample was again placed on the spinner and this process was repeated 10–30 times, depending on the final thickness desired. The multicoated samples were then put into a furnace with flowing $O_2$, heated to 900 °C for 5 min, cooled at 2 °C min$^{-1}$ to 400 °C, held at 400 °C for 6 h, and then slowly cooled to room temperature. These sintered samples were examined with light microscopy, scanning electron microscopy (SEM), X-ray diffraction, a SQUID magnetometer and a surface profilometer to measure the surface roughness.

3. Experimental results and discussion

Initially, we attempted to use the metal nitrates $[M^{n+}(NO_3)_x, M = Y, Ba$ or Cu] instead of the acetates as the starting materials to minimize the amount of excess carbon introduced into the solution. With an identical molarity and acid/alcohol ratio as was used with the acetates, it was difficult to maintain a clear solution due to the copious precipitation of $Ba(NO_3)_2$. Unless ammonium hydroxide (NH$_2$OH) was added to adjust the pH to a neutral value (pH 7–9), precipitation problems arose, which has also been encountered by other workers [11, 12]. Along with premature precipitation due to evaporation of NH$_2$OH under normal experimental conditions, the solution was further diluted by the water formation from the acid–base reaction. Although the amount of excess carbon introduced into the sample is increased with the use of acetates, it is only by 6.5% over the nitrates.

Figure 1 shows the TGA curve for the solution. The majority of the weight loss occurred below 500 °C with only a 0.16% loss between 500 and 900 °C. These results were the basis for choosing 500 °C as the volatilization temperature for the as-deposited films. The initial weight loss, from 50 to 150 °C, is due to the evaporation of water and the subsequent loss from 150 to 500 °C is due to the removal of the organic compounds. The final weight loss occurring between 900 and 1000 °C is due to persistent carbonaceous species.

The DTA curve in Fig. 2 shows a lone exothermic peak occurring at 420 °C. This peak represents the removal of the final organic compounds by oxidation [12] and is corroborated by the TGA results. We could not identify an exothermic peak which would correspond to the nucleation or crystallization of the amorphous gel. There are numerous studies of the citrate decomposition technique [8, 10–14], but exotherms related to the crystallization temperature were not found.

Figure 3(a)–(c) shows the X-ray diffraction patterns taken from the solution heated at 500 °C for 2 min, 500 °C for 20 min and 950 °C for 1 h respectively. As shown, for the sample heated for only 2 min at 500 °C, only an amorphous phase is present while at 20 min some crystallinity is evident. This is due to the extreme sensitivity of the prefired films to environmental conditions. These peaks correspond to $BaO$, CuO and $BaCuO_2$ but no peaks were identified for any yttrium compounds. Coppa et al. [15] and Chu and Dunn [10] report similar crystallinity in materials synthesized with nitrate precursors. This indicates that yttrium is more stable in the prefired films and does not react significantly with the atmosphere. The superconducting phase also developed in the same chemical sequence as in
the powders formed by decomposition of the solution. X-ray diffraction patterns taken at the different temperatures are identical for substrate and powders. Figure 4 shows the X-ray diffraction pattern taken from the single crystal MgO substrate after sintering at 900 °C in O₂ which clearly shows that only the orthorhombic phase is present.

Surface adhesion was initially a problem which was remedied by a variety of techniques. The optimal surface cleaning treatment involved hot ultrasonicating with the RBS-35™ cleaner. If only standard solvents were used, the solutions would not spread evenly on the substrates. The viscosity of the solution was also a major factor in the film quality. If the solution was too

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Fig. 3. X-ray diffraction patterns taken from the precursor solution heated to (a) 500 °C for 2 min, (b) 500 °C for 20 min, (c) 950 °C for 1 h.
viscous, it would clump and not spread evenly. If the solution was too fluid, each coating was very thin and a prohibitive number of coatings had to be applied. The optimal molarity (in total metal cations) was found to be \( \approx 3 \) M.

The film thickness ranged from 0.5 to 1.5 \( \mu \)m, depending on how many coats were applied. All of the films appeared quite smooth and not much porosity was evident. Figure 5(a) is an SEM micrograph showing the film on the silver substrate and Fig. 5(b) is a higher magnification showing the extremely fine grain size \( (<1 \mu m) \) of the material. We attribute the small grain size to the limited time the sample is exposed to high temperatures: 5 min at 900 °C. There was some cracking evident in the sapphire and MgO films, which is likely to be due to thermal mismatch.

Figure 6 is a SQUID magnetometer trace showing the superconducting transition for the stabilized ZrO\(_2\) substrate. The onset is \( \approx 89 \) K and the transition width is large. The poor superconducting behavior is partially due to the high field used but it is also an indication of the second phases present in our films, also detected by X-ray diffraction.

Figure 7 shows the profilometer trace on the sapphire substrate for two differently processed films. A film prepared by a screen printing technique was compared with the chemically processed films. The average distance between the peaks and valleys of the spun-on coatings was about five times lower than that of the screen printed films, as shown in Fig. 7(a) and (b). This indicates that the spun-on films would presumably show better electrical properties when attached to other components. The profilometer trace of a pure sapphire substrate shows no detectable roughness on the scale in which we were measuring.
4. Conclusions

Smooth, continuous surfaces of the YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor can be fabricated by decomposition of organic gels. High molarity solutions can be used without undesirable precipitation if the precursor compounds are the metal acetates. Prefiring the as-deposited films results in the development of thick layers in a short amount of time without the appearance of bubble formation or surface cracks. Barium and copper in the prefired films form oxide complexes after exposure to the atmosphere, but these contaminants can be removed by a 500 °C anneal. The first crystalline phase to nucleate in the amorphous gel upon heating is not the orthorhombic phase, which develops at higher temperatures. The surfaces of the films are smooth and continuous with no evidence of substrate cohesion problems with the single-crystal magnesia and sapphire or the polycrystalline zirconia and silver. The grain size of the films is \( \approx 1 \, \mu \text{m} \) attributed to the short annealing time at high temperatures. The surfaces have an average roughness which is much less than for another film sample prepared by screen printing.

Acknowledgments

The authors wish to thank the General Atomics Corporation, San Diego for financial assistance and thank K. S. Mazdiyasni and Fred Montgomery for helpful discussions. We also thank Huey-Lin Luo for the use of his screen printed film.

References