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Superconducting Films Prepared Using the Metallo-Organic Decomposition Technique

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Many of the proposed applications of the new high-T_c superconductors in the rare-earth–alkaline earth–copper–oxygen system require that the material be deposited in thin film form on a suitable substrate. Numerous papers have been published in the last year on the properties of high-T_c superconducting films prepared by classical techniques, such as evaporation and sputtering. In this note we discuss the application of the metallo-organic decomposition (MOD) technique, developed at Purdue University (*1–5*) as a simple method for film deposition, to the preparation of superconducting $YBa_2Cu_3O_{7-\delta}$ films. The structure and properties of the films so produced, already briefly described earlier (*6*), are also discussed.

The MOD process involves dissolving metallo-organic compounds of the individual elements in an appropriate solvent, mixing the solutions to achieve the desired stoichiometry, adjusting the rheology, depositing these formulations on an appropriate substrate to make a film, and then firing these wet films to obtain the desired inorganic film. The metallo-organic compounds used in this study were the 2-ethylhexanoates of yttrium and copper and the neodecanoate of barium. The yttrium and

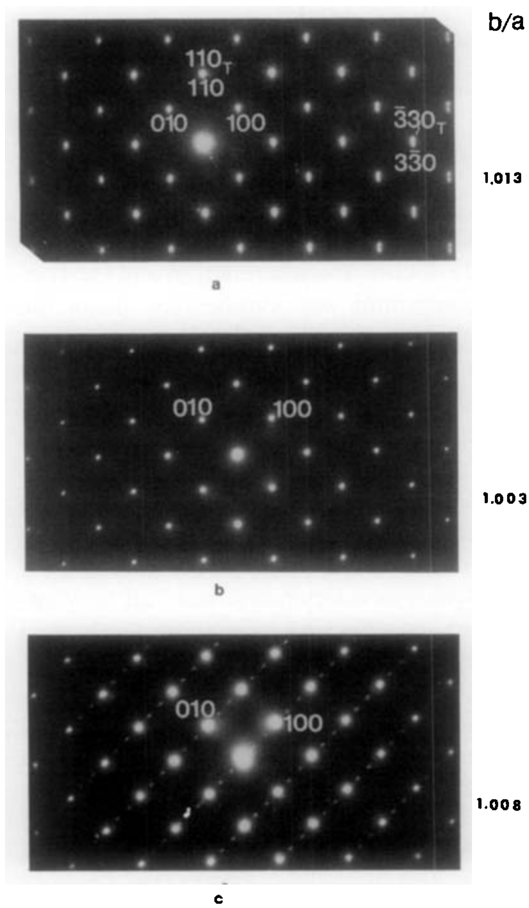

FIG. 1. Electron diffraction patterns from three grains in a MOD film of $YBa_3Cu_3O_{7-\delta}$.

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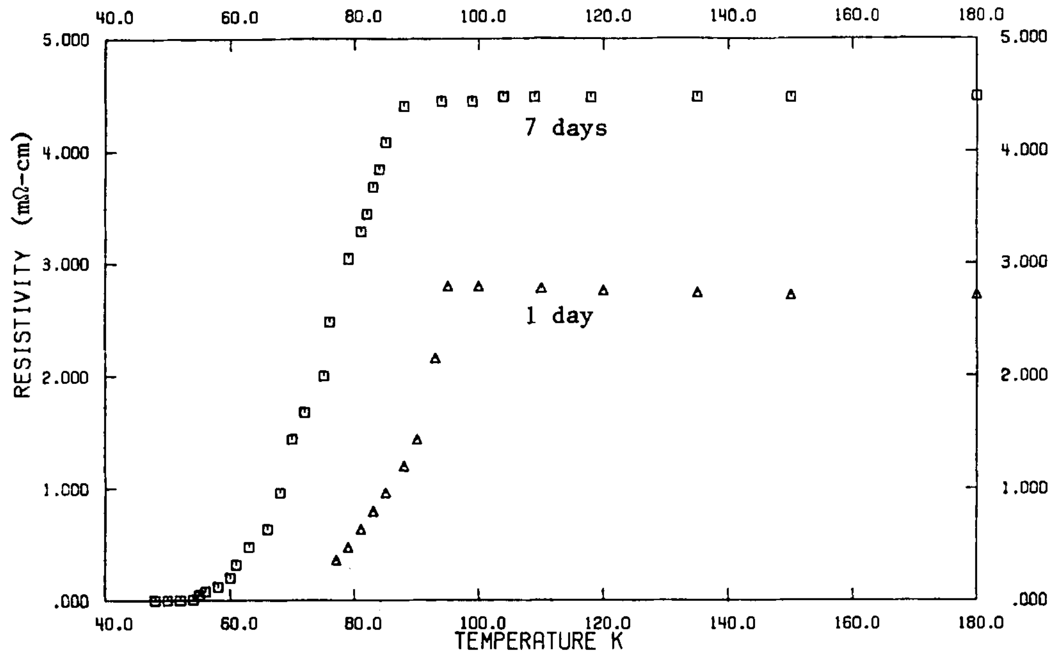

FIG. 2. Resistivity of a 2-μm MOD film of $YBa_3Cu_3O_{7-\delta}$ on sapphire measured 1 and 7 days after fabrication.

barium compounds were synthesized by the double decomposition reaction and the copper compound was synthesized using the Metathesis reaction following the procedures previously reported (7). The compounds were dissolved in xylene to produce a formulation that yielded 9 wt% $YBa_2Cu_3O_7$ on thermal decomposition. This formulation was spun onto sapphire substrates and heated to pyrolyze the film. It was determined that the temperature, heating rate, and pyrolysis temperature were all very important in effecting the superconducting properties of the films. Films are currently being pyrolyzed by heating at 30°C per minute in flowing oxygen to 850°C. The typical single-layer fired film thickness was 200 nm; the deposition and pyrolysis steps were repeated up to 10 times to give the desired film thickness. The films were then given a final anneal in oxygen at 920°C for 1 hr and furnace cooled.

Observations with the scanning electron microscope showed the films to be very dense and crack free without pin holes. X-ray diffraction studies confirmed that the films were orthorhombic with very little preferred orientation. Electron diffraction studies[1] of individual grains showed a variation in the *b*/*a* ratio from grain to grain, as previously reported (*8*) for bulk material, but in all cases *b*/*a* was less than the X-ray value of 1.017 (*8*). Figure 1 shows electron diffraction patterns from three grains taken with the [001] beam incidence, and also specifies the *b*/*a* values for the grains. The elongation of the spots in Fig. 1(a) are indicative of (110) type of microtwins. Additional spots in the *a* direction (Fig. 1(c)) were observed in a few grains and indicate a periodic structure every three unit cells in

[1] The authors express their appreciation to Professor Y. Hirotsu of the Technological University of Nagaoka, Nagaoka, Japan, for conducting the electron diffraction experiments.

the *a* direction; one possible explanation is an ordering of oxygen vacancies.

Measurements of resistivity versus temperature of the MOD films showed a rather broad transition from the normal to the superconducting state, and also indicated a detrimental interaction between the film and the atmosphere. Figure 2 shows 4-terminal resistivity results for the same film measured 1 and 7 days after preparation. The film had a superconducting onset temperature below 90 K and a zero-resistance temperature of 55 K after exposure to the atmosphere for 7 days, whereas the onset temperature was greater than 90 K when measured 1 day after preparation. Resistivity measurements of the film 1 day after preparation were only carried to 77 K, but it appears that the temperature of zero-resistance would have been approximately 70 K. Figure 2 also shows that the 100 K resistivity increased 60% between 1 and 7 days exposure to the atmosphere.

In summary, dense and uniform films 0.2 to 2 μm thick of $YBa_2Cu_3O_{7-\delta}$ can be prepared by the MOD process, although optimum processing conditions have not as yet been established. The superconducting properties are detrimentally affected by exposure to the atmosphere, which indicates that passivation of the films will be required.

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