2-20-1989

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Highly oriented Ti$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ thin films by pulsed laser evaporation

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(Received 7 November 1988; accepted for publication 20 December 1988)

We have fabricated superconducting thin films on MgO(100) substrates with nearly pure Ti$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ (2:2:2:3) phase using pulsed laser evaporation and post-annealing. The films had c axes perpendicular to the substrates. Superconducting films with onset temperatures of 125 K and zero resistance at 110 K were obtained. X-ray microprobe fluorescence measurements indicate that a typical composition of films is Ti$_{0.66}$Ba$_{1.77}$Ca$_{1.46}$Cu$_{3}$O$_{10}$, which is low in Ti compared to that expected for the 2:2:2:3 phase. A typical grain size is greater than 10 μm as revealed by scanning electron microscopy.

The discoveries of high $T_c$ superconductivity in the rare-earth-free Bi-Sr-Ca-Cu-O and Ti-Ba-Ca-Cu-O systems have stimulated considerable new research. In the Ti-based system, the following superconducting phases have been identified: Ti$_{1.7}$Ba$_2$Ca$_{0.8}$Cu$_{2.3}$O$_{5+n}$ and Ti$_2$Ba$_2$Ca$_{1-n}$Cu$_{2.3}$O$_{5+n}$ ($n = 1-5$). These superconductors possess a crystal structure similar to the layered perovskite oxide arrangement. The superconducting properties of these phases vary greatly with the number of copper oxide layers. $T_c$'s up to 125 K have been achieved in the bulk sample of Ti$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ (2:2:2:3).

Recently, Ti-based films have been prepared by electron beam evaporation and single-target or multihot sputtering. Ginley et al. reported a transport $J_c$ above $2.4 \times 10^5$ A/cm$^2$ at 77 K for unoriented 2:2:2:3 phase films, with little magnetic field dependence observed. Lee et al. have achieved $T_c$'s of up to 120 K in oriented multiphased films. Critical current densities ($J_c$) as high as $1 \times 10^5$ A/cm$^2$ at 100 K in zero magnetic field have been reported by Hong et al. on a SrTiO$_3$ substrate with the oriented 2:2:2:3 phase. Pulsed laser deposition has been proven to produce high quality YBa$_2$Cu$_3$O$_y$ superconducting films. In this technique, high quality films could be produced by using a small target in a sealed environment which is important for the study of toxic material such as Ti-based compounds. In this letter, we describe the synthesis of highly textured, c axis oriented, Ti$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ thin films with a $T_c$ onset at 125 K and zero resistance below 110 K, using pulsed laser evaporation and post-annealing.

Ti-Ba-Ca-Cu-O films were deposited onto MgO(100) substrates at ambient temperature using a 2 Hz, 1.22 J/cm$^2$ pulse from a frequency-doubled Nd:YAG laser operating at 532 nm. The target was a composite of Ti$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ made by sintering a mixture of Ti$_2$O$_3$, BaO, CaO, and CuO with a metal cation 2:2:2:3 ratio. The as-deposited films, about 1 μm thick, were not conducting, and a post-annealing step at 840-900 °C was applied to make them superconducting. Post-annealing of films was carried out under 1 atm of O$_2$ or air in a sealed quartz tube. The procedure was similar to that used by Lee et al., but the annealing temperature of our best films was lower than theirs by about 30 °C. The film compositions were determined by x-ray fluorescence microprobe spectroscopy. An average composition of as-deposited film was Ti$_{0.5}$Ba$_{1.8}$Ca$_{1.95}$Cu$_{3}$O$_y$. A typical film composition after annealing was Ti$_{0.66}$Ba$_{1.77}$Ca$_{1.46}$Cu$_{3}$O$_{10}$. The film composition was not homogeneous, especially, in the Ti content which was found to vary within a range of about 20% from place to place over the film surface.

The crystal structure of each annealed film was characterized by x-ray diffraction. A Rigaku θ-2θ diffractometer with Cu K$_α$ radiation was used. The phases formed in the films depended strongly on the heat treatment conditions, such as temperature and the duration of the reaction time. The x-ray diffraction patterns for films annealed at 870°C for 5 and 10 min are shown in Fig. 1. For films that were heat treated less than 10 min at 870 °C or below 870 °C, the phases were mixed. As shown in Fig. 1(a), a film an-

![FIG. 1. X-ray diffraction pattern of Ti-Ba-Ca-Cu-O films on MgO substrates (a) annealed at 870 °C for 5 min which contained mostly 2:2:2:3 and 2:2:1:2 phases. Some (006) peaks of the 2:2:1:2 phase are indexed; (b) annealed at 870 °C for 10 min which contained a nearly pure 2:2:2:3 phase. (006) peaks of the 2:2:2:3 phase are indexed.](image-url)
nealed at 870 °C for 5 min contained typically both 2:2:1:2 and 2:2:2:3 phases. The major peaks can be assigned to the diffraction from the c plane with lattice constants of c = 29.3 and 35.6 Å. This mixed-phase film is highly oriented, with the c axis perpendicular to the film plane. For the films annealed at 870 °C for 10-30 min, the 2:2:2:3 becomes the primary phase. In Fig. 1 (b) sharp periodic peaks were observed in the pattern. This indicates that the film is highly oriented. All peaks can be assigned to the (00l) peak of the 2:2:2:3 phase.

Superconducting and transport properties were measured using the standard four-point measurement technique with d.c. currents, where the polarization of the current was switched during the measurements. The resistivities were estimated using the van der Pauw method, and the values lay between 500 and 1500 ¡

The transport critical current density of this film was evaluated to be 10³ A/cm² at 77 K in a zero magnetic field. This value of the critical current density is lower than the best results that were reported. This may be partly due to the porosity of the present sample.

The morphology of these films was studied by scanning electron microscopy. Scanning electron micrographs of a typical sample on a MgO(100) substrate before and after heat treatment are shown in Fig. 3. The as-deposited film has a grain size of about 1 µm and the surface is somewhat rough, as shown in Fig. 3(a). Figure 3(b) shows a scanning electron micrograph of the surface of a film annealed at 870 °C for 10 min. The growth of platelets parallel to the substrate is evident in the micrograph. The grains are typically 10 µm in diameter and are poorly connected. Energy dispersive x-ray microanalysis of the surface of these films revealed broad compositional inhomogeneities, especially in the Ti content which varied from point to point. There were many pinholes which contained very little Ti compound. This indicates that the Ti compound may not wet the MgO substrate very well. Based on these observations, we may be able to increase Jc by improving the wetting of the substrate, and morphology of the film.

In summary, we have prepared Ti-Ba-Ca-Cu-O thin films on MgO(100) substrates using pulsed laser evaporation. The microstructure of the film is dependent on the post-annealing conditions. Nearly single phase films of Ti$_2$Ba$_2$Ca$_2$Cu$_{10}$O$_{10}$ on MgO substrates are routinely obtained by keeping the same post-annealing conditions. Superconducting films with Tc onset at 125 K and Tc (R = 0) = 110 K have been achieved. Future work will be concentrated on improving the morphology and producing films with a higher Jc.

We would like to thank Professor D. J. Sellmyer for providing a furnace. This work is supported in part by NASA Lewis grant NAG 3-866.


