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

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We have fabricated superconducting thin films on $\text{MgO}(100)$ substrates with nearly pure $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (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 $\text{Ti}_{0.66}\text{Ba}_{1.77}\text{Ca}_{1.46}\text{Cu}_3\text{O}_x$, which is low in Ti compared to that expected for the 2:2:2:3 phase. A typical grain size is greater than $10\text{ }\mu\text{m}$ 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.¹⁻⁷ In the Ti-based system, the following superconducting phases have been identified: $\text{TiBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ and $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1-5$). 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 $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2:2:2:3).³

Recently, Ti-based films have been prepared by electron beam evaporation⁸ and single-target^{9,12} or multitarget^{13,14} sputtering. Ginley *et al.*⁸ reported a transport J_c above $2.4 \times 10^5\text{ A/cm}^2$ 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.⁹ Critical current densities (J_c) as high as $1 \times 10^5\text{ A/cm}^2$ at 100 K in zero magnetic field have been reported by Hong *et al.*¹² on a SrTiO_3 substrate with the oriented 2:2:2:3 phase. Pulsed laser deposition has been proven to produce high quality $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconducting films.^{15,16} 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, $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ 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 $\text{MgO}(100)$ substrates at ambient temperature using a 2 Hz, 1.22 J/cm² pulse from a frequency-doubled Nd:YAG laser operating at 532 nm. The target was a composite of Ti-Ba-Ca-Cu-O made by sintering a mixture of Ti_2O_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.*,⁹ 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 $\text{Ti}_{0.5}\text{Ba}_{1.8}\text{Ca}_{1.95}\text{Cu}_3\text{O}_x$. A typical film composition after annealing was $\text{Ti}_{0.66}\text{Ba}_{1.77}\text{Ca}_{1.46}\text{Cu}_3\text{O}_x$. 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 -2 θ diffractometer with $\text{Cu K}\alpha$ 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 (00 l) 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. (00 l) peaks of the 2:2:2:3 phase are indexed.

FIG. 2. Resistance vs temperature for a Tl-Ba-Ca-Cu-O film on MgO annealed at 870 °C for 10 min.

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 (00 l) peak of the 2:2:2:3 phase.

Superconducting and transport properties were measured using the standard four-point measurement technique with dc 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 $1500 \mu\Omega \cdot \text{cm}$. These values are considerably higher than $\text{YBa}_2\text{Cu}_3\text{O}_7$ and Bi-based superconductors. However, if we take into account the porosity and roughness of these films the actual resistivity of Tl-based superconductors may be much smaller. (The evidence of porosity and roughness of the films is discussed later.) Figure 2 shows the resistivity versus temperature characteristics observed for the annealed sample with a nearly pure 2:2:2:3 phase. The superconducting transition for this film started around 125 K, and its zero-resistance state was achieved below 110 K. The transport critical current density of this film was evaluated to be 10^4 A/cm^2 at 77 K in a zero magnetic field. This value of the critical current density is lower than the best results that were reported.^{8,12} 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 $1 \mu\text{m}$ 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 $10 \mu\text{m}$ in diameter and are poorly connected. Energy dispersive x-ray microanalysis of the surface of these films revealed broad compositional inhomogeneities, especially in

FIG. 3. Scanning electron micrograph of the same films as in Fig. 2: (a) as-deposited and (b) after annealing at 870 °C for 10 min.

the Tl content which varied from point to point. There were many pinholes which contained very little Tl compound. This indicates that the Tl compound may not wet the MgO substrate very well. Based on these observations, we may be able to increase J_c by improving the wetting of the substrate, and morphology of the film.

In summary, we have prepared Tl-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 $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ on MgO substrates are routinely obtained by keeping the same post-annealing conditions. Superconducting films with T_c onset at 125 K and $T_c(R=0) = 110$ K have been achieved. Future work will be concentrated on improving the morphology and producing films with a higher J_c .

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