November 1988

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(Received 11 August 1988; accepted for publication 28 September 1988)

Superconducting Tl-Ba-Ca-Cu-O thin films 0.2–1.0 μm thick have been prepared on MgO(100) and $SrTiO_3$(100) substrates by dc diode sputtering using a single oxide target. Films containing primarily the $Tl_2Ba_2Ca_1Cu_2O_8$ phase were obtained with a T_c ($R = 0$) at 102 K and a transport J_c of 10^4 A/cm^2 at 90 K. For the nearly pure phase $Tl_2Ba_2Ca_2Cu_3O_{10}$ films, the T_c's ($R = 0$) are higher at 116 K and the transport J_c's at 100 K are of 10^5 A/cm^2. Both types of films show a strong preferred orientation with the c axis perpendicular to the film plane. The rocking curve of the $Tl_2Ba_2Ca_2Cu_3O_{10}$ films is 0.32° wide and the typical grain size is over 10 μm.

The recent discovery of rare-earth-free high T_c superconductors in Bi-Sr-Ca-Cu-O[1] and Tl-Ba-Ca-Cu-O[2] systems has created much excitement because of the achievement of high T_c's up to 125 K. Both the Bi- and Tl-bearing superconducting phases possess similar crystal structures as a layered perovskite oxide arrangement.[3,4] In the Tl-based system, three superconducting phases have been observed and identified as $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ for $n = 1$, 2, and 3.[4] The T_c's of bulk ceramics are 80, 110, and 125 K for $n = 1$, 2, and 3, respectively. The crystal structure of the highest T_c compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2:2:2:3 phase) is tetragonal, with lattice constants $a = 3.85$ Å and $c = 35.9$ Å. It consists of alternating the Ba-Cu-Ca-Cu-Ca-Cu-Ba perovskite oxide slabs with a double thallium-oxygen layer giving a layer repeat sequence of ...Tl-Tl-Ba-Cu-Ca-Cu-Ca-Cu-Ba... along the c direction.[4] The other high T_c phases 2:2:1:2 and 2:2:0:1 are similarly constructed with fewer pairs of Cu-Ca layers.

Thin-film studies of the high T_c Tl-based oxide superconductors are particularly important considering the prospect of achieving stable critical current densities J_c's in excess of 10^5–10^6 A/cm^2 at 77 K. Earlier, unoriented polycrystalline Tl-Ba-Ca-Cu-O films with T_c ($R = 0$) at 97 K and J_c (77 K) of 10^5 A/cm^2 have been obtained by Ginley *et al.*[5] using electron beam evaporation 2:2:1:2 single-phase films with T_c ($R = 0$) at 102 K and J_c (77 K) of 10^5 A/cm^2 by Ichikawa *et al.*[6] using single-target magnetron sputtering, and more recently, films containing 2:2:2:3 phase with T_c ($R = 0$) at 120 K and J_c (77 K) of 10^4 A/cm^2 by Lee *et al.*[7] using rf diode sputtering. Here, we report the preparation and characterizations (structural and superconducting properties) of superconducting Tl-Ba-Ca-Cu-O thin films by a simple dc diode sputtering technique. We have reproducibly made highly c-axis oriented superconducting films 0.2–1.0 μm thick on both MgO(100) and $SrTiO_3$(100) single-crystal substrates with a major phase being either 2:2:2:3 or 2:2:1:2 depending on the heat treatments. The 2:2:2:3 films have a T_c onset of 125 K and a T_c ($R = 0$) at 116 K, while for films containing 2:2:1:2 phase, T_c onset is about 110 K and T_c ($R = 0$) is 102 K. The transport critical current densities at zero magnetic field are high for both types of films: they are over 10^4 A/cm^2 at 90 K and 10^5 A/cm^2 at 77 K for the 2:2:1:2 films. For the 2:2:2:3 films, the J_c's are significantly higher than the values reported previously, i.e., over 10^4 A/cm^2 at 110 K and 10^5 A/cm^2 at 100 K. The 2:2:2:3 films are single phase and are of high quality with a narrow rocking curve 0.32° wide.

The film deposition was carried out by a dc diode getter sputtering technique.[8] Pure argon sputtering was used with the pressure kept at 80 mTorr during deposition. Film deposition using a lower argon pressure of 30 mTorr is now in progress to determine the effect of the argon pressure during sputtering. No partial oxygen pressure was added. A background pressure of 2×10^{-7} Torr was achieved prior to the introduction of argon. Each target was presputtered for 10 h to ensure that the target surface had reached an equilibrium condition before the first film deposition. Afterwards, a 60 min presputtering was always used before each run. Both single-crystal $SrTiO_3$ and MgO substrates with a (100) orientation were used. The substrate-to-target distance was chosen to be 16 mm. The deposition rate was 3.5 nm/min with an output power of 3 W. The thickness of the films ranges from 0.2 to 1.0 μm. Some very thin films 0.03 μm thick were also made for the determination of film composition. Note that several 0.03-μm-thick films were made randomly during the course of this study to ensure the consistency in film composition from run to run. The result showed that using a single oxide target, we always obtain films with the same composition. The substrate holder during deposition was kept at room temperature. The composition of Tl-based targets does not change significantly even after very long usage (more than 300 h). During the film deposition, the plasma is confined in a liquid-nitrogen-cooled stainless-steel can, therefore eliminating the contamination of the Tl or Tl oxides over the entire vacuum chamber.

The oxide targets were prepared from thallium oxide, copper oxide, barium carbonate, and calcium carbonate powders with a nominal (metal cation) compositional ratio of 8:2:2:3 of Tl:Ba:Ca:Cu. Appropriate amounts of powders were mixed in a fume hood, cold pressed into a disk-shaped plate 2.5 cm in diameter and 0.3 cm thick at a pressure of 1.5 tons/cm^2. The pressed plate was wrapped in a gold foil,

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 0003-6951/88/472102-03$01.00

reacted at 880 °C for 3 h in a sealed quartz tube, and then cooled to room temperature for 2 h. The step of wrapping the target in a gold foil is necessary in order to prevent the interaction between the target and the quartz tube during the high-temperature annealing. The nominal target composition after the reaction is 2.3:2:2:3:x of Tl:Ba:Ca:Cu:O. This composition was obtained by assuming that the loss of the material is due to Tl oxide. The target was conducting at room temperature.

The actual film composition was determined by Rutherford backscattering spectrometry (RBS) using 1.8 MeV He^+ ions. A typical spectrum with the He ion beam at normal incidence is shown in Fig. 1 for an unreacted sample 0.03 μm thick. Single-crystal MgO(100) substrates were used in this measurement. Samples with very thin thickness were chosen such that the peaks in the RBS spectrum are well separated. Therefore, a more accurate determination of the four metal constituents can be made. The stoichiometry of the films is determined to be 2:1.86:2.08:3.04:x of Tl:Ba:Ca:Cu:O. A small amount (less than 1%) of argon was detected in the as-deposited films as shown in Fig. 1.

The as-deposited films are amorphous and insulating, and need a post-deposition anneal to become superconducting. In order to prevent further loss of Tl or other elements, films were wrapped in a gold foil with pellets of compressed composite Tl-Ba-Ca-Cu oxide powders and sealed in a quartz tube. The general heat treatment procedure is similar to that used by Lee *et al.*,[7] except that the temperature is lower as described below. The quartz tube was filled with 1 atm of O_2 or air. The films were then annealed at temperatures between 800 and 880 °C for various periods of time (from 5 min to several hours depending on the annealing temperature) and then furnace cooled to room temperature in about 3 h. There is no apparent difference in superconducting properties for the Tl-based films heat treated under air or oxygen atmosphere.

The crystal structure of the annealed films was characterized by x-ray diffraction. A Philips θ-2θ diffractometer with Cu K_α radiation was used. The phase formation of 2:2:1:2 or 2:2:2:3, in fact, depends very much on the heat treatment conditions such as the temperature and the duration of the reaction time. For films heat treated below 860 °C, or reacted at a very short period of time at 870 °C ($\sim$5 min), primarily 2:2:1:2 phase, an amorphous region, and some minor phases were observed as shown in Fig. 2(a). These films are textured with the c axis perpendicular to the film plane. All the major peaks can be assigned to the 2:2:1:2 phase with the lattice constant $c = 29.3$ Å.

However, when the films with the same composition were heat treated at 870 °C for 10–30 min, the 2:2:2:3 become the primary phase. In Fig. 2(b), the periodical sharp peaks observed in the x-ray diffraction pattern (θ-2θ scan) are the (00l) peaks of the 2:2:2:3 phase with the lattice constant of $c = 35.6$ Å, a value close to that reported in the 2:2:2:3 phase of Tl-Ba-Ca-Cu-O bulk ceramics.[4] For the measurements of rocking curves, a triple-axis four-circle diffractometer with a 12 kW rotating Cu anode source was used. A pair of perfect, flat Ge(111) monochromator and analyzer crystals was used to provide a spatial resolution of 3×10^{-5} Å^{-1} for the rocking scans. We found that the full width at half maximum (FWHM) of the rocking curve normal to the film plane is 0.32° for the 2:2:2:3 films on MgO(100) substrates. There appeared to be no in-plane order of the films with respect to the MgO crystal. Our Tl-Ba-Ca-Cu-O films with a major phase of the high T_c 2:2:2:3 compound have been obtained routinely (at least 30 films with a yield of almost 100%) on both MgO(100) and $SrTiO_3$(100) single-crystal substrates. The films are also stable in air.

The superconducting and transport properties were measured by the standard four-point measurement using a dc method by switching the polarization of the applied current during the measurement. The applied current in the dc method is usually around 2.5–100 μA. For the films containing the 2:2:1:2 phase, they in general exhibit a relatively high room-temperature resistivity of 500–1000 $\mu\Omega$ cm due to the existence of nonsuperconducting phases. A typical resistivity versus temperature curve for this type of films is shown in Fig. 3(a) for T_c ($R = 0$) at 102 K. The critical current den-

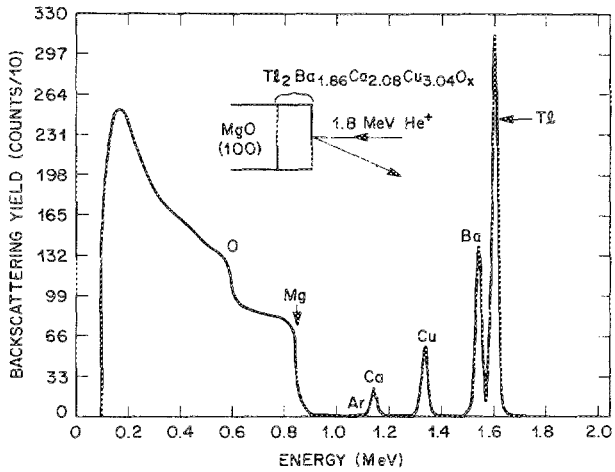

FIG. 1. Rutherford backscattering spectrum for a 0.03-μm-thick $Tl_2Ba_{1.86}Ca_{2.08}Cu_{3.04}O_x$ film on MgO(100) by sputtering.

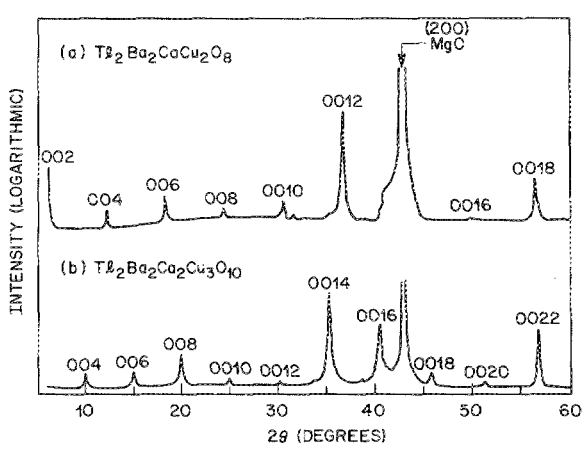

FIG. 2. X-ray θ-2θ scans normal to the film for (a) Tl-Ba-Ca-Cu-O film containing primarily 2:2:1:2 phase on MgO(100), (b) pure 2:2:2:3 phase Tl-Ba-Ca-Cu-O film on MgO(100).

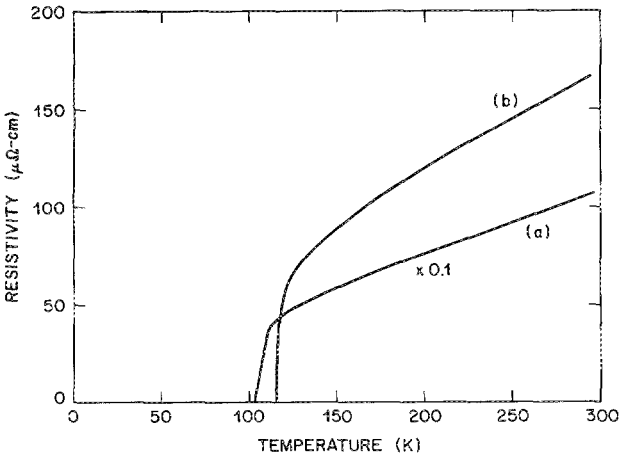

FIG. 3. Resistivity vs temperature curves (a) for the same as in Figs. 2(a) and (b) for the same film as Fig. 2(b).

sity J_c for this film, measured by the dc transport method at zero magnetic field, is 10^4 A/cm^2 at 90 K and 10^5 A/cm^2 at 77 K, comparable to the values reported by Ginley *et al.*[5] and Ichikawa *et al.*[6]

For the films containing only the 2:2:2:3 phase [see Fig. 2(b)], the room-temperature resistivity is much lower, about 100–300 $\mu\Omega$ cm. Also, the T_c's ($R = 0$) are higher at 116 K. The T_c values are similar for the films deposited on MgO(100) or $SrTiO_3$(100) substrates. Figure 3(b) shows the resistivity versus temperature curve for the film 0.4 μm thick deposited on MgO(100). The transport J_c's at zero magnetic field for the 2:2:2:3 films on $SrTiO_3$(100) are high: 10^4 A/cm^2 at 110 K and 10^5 A/cm^2 at 100 K. J_c's carried by the films deposited on $SrTiO_3$(100) are slightly higher than those by the films on MgO(100), presumably due to a different morphology as revealed by a scanning electron microscopy (SEM) study. The SEM results are published elsewhere.[9]

In summary, we have routinely produced, by a simple dc diode sputtering technique, superconducting Tl-Ba-Ca-Cu-O films on both MgO(100) and $SrTiO_3$(100) substrates. For films with the same as-deposited composition, both the 2:2:1:2 phase with T_c ($R = 0$) at 102 K and the 2:2:2:3 phase with T_c ($R = 0$) at 116 K have been obtained solely depending on the heat treatment conditions. The transport J_c's are higher for the 2:2:2:3 films: 10^5 A/cm^2 at 100 K and zero magnetic field.

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