EPITAXIAL GROWTH OF HIGH-\(T_c\) SUPERCONDUCTING TI-Ca-Ba-Cu-O FILMS BY LIQUID PHASE EPITAXIAL PROCESS

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TI-Ca-Ba-Cu-O epitaxial films have been successfully grown on (001) MgO substrate by liquid phase epitaxial (LPE) process. The as-grown films showed an onset of superconductivity at about 140 K and zero resistance at 111 K. X-ray diffraction analysis suggests the film to be highly preferentially oriented with the c-axis perpendicular to the film surface. Observation from transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) revealed the presence of both TI-Ca2Ba2Cu3Oy and TiCa2Ba3Cu4Oy phases.

1. Introduction

Recently, TI-Ca-Ba-Cu-O superconducting films have been prepared by RF sputtering [1], multtarget magnetron sputtering [2], electron beam evaporation [3] and symmetric RF diode sputtering [4]. These films (TCBCO) are of interest since they, similar to Bi-Ca-Sr-Cu-O (BCSCO) films, do not require the presence of a rare earth element for superconductivity. The quarternary nature of both TCBCO and BCSCO systems makes co-evaporation and various sputtering techniques difficult for their synthesis. In a previous study, we have grown epitaxial BCSCO films on (001) MgO substrate by the liquid phase epitaxial (LPE) process. A zero resistivity temperature of 81 K was obtained [5,6]. In this paper, we report the synthesis of highly textured TCBCO superconducting films by LPE. Electrical resistivity of the film grown was carried out by a standard four-probe method. Transmission electron microscopy (TEM) and energy dispersive spectrometry (EDS) as well as X-ray diffraction were used to determine the crystal structures of the superconducting phases.

2. Experimental

All the reagents used in this research were high purity Ti2O3, CaCO3, BaCO3 and CuO. The nominal composition of powder as a melt for LPE processing was Ti:Ca:Ba:Cu = 1.33:1.33:1.00:2.00. The CaCO3, BaCO3 and CuO powders were mixed and calcined at 920–930°C for 10–15 h in air before mixing with Ti2O3. The prepared powder and MgO substrate were arranged in a gold boat, then put into the loaded furnace at 930–950°C for 0.5–1 h for equilibration of the melt. To alleviate possible decomposition of Ti2O3 to TiO2 and O2 under the synthesis condition, the process was performed in flowing O2 and with a tight lid above the gold boat. The reactor boat was then tipped for the melt to contact with MgO substrate for 10–20 min. The furnace was cooled to about 890°C at 0.3–1°C/min and the remaining liquid solution was removed by gravity. Subsequently, the furnace was allowed to cool down to room temperature. After that, the films with a thickness of 40–80 µm were taken out without further heat treatment. This LPE growth process was similar to that used for BCSCO that we have reported previously [5].

A standard four-point probe was used for electrical resistance measurement. Electrical contacts were attached to the sample by fine copper wires with conductive silver paint. A JEOL-2000FX transmis-
3. Results and discussion

The scanning electron micrograph in fig. 1 shows a flat terrace-like surface. The X-ray diffraction pattern, shown in fig. 2, indicates the c axis being perpendicular to the (001) plane of the MgO substrate. EDS analysis shows the film compositions to be TlCa₂Ba₂Cu₃O₇ (major phase) and TlCa₂Ba₃Cu₄O₇ (minor phase). TEM analysis identifies the TlCa₂Ba₃Cu₄O₇ phase to be of P4/mmm space group with a=b=0.39 nm and c=1.97 nm [7]. The crystal structure of TlCa₂Ba₃Cu₄O₇ is similar to that of TlCa₂Ba₃Cu₄O₇.

A probable structure model for TlCa₂Ba₃Cu₄O₇ is proposed to contain four Cu-O layers. The sequence of cations along the c axis is suggested to be Tl-Ba-Ca-Cu-Cu-Ba-Ca-Cu-Ba-Tl. In the case of TlCa₂Ba₃Cu₄O₇, the possible sequence is Tl-Ba-Ca-Cu-Ca-Cu-Ca-Cu-Ba-Tl with three Cu-O layers. Analyses of X-ray diffraction patterns and SEM/EDS results revealed that both TlCa₂Ba₂Cu₃O₇ and TlCa₂Ba₃Cu₄O₇ were highly (001) preferentially oriented in the LPE as-grown films.

Fig. 1. Scanning electron micrograph of a LPE as-grown film.

Fig. 2. X-ray diffraction pattern showing the (00l) preferred orientation of TlCa₂Ba₂Cu₃O₇ (Mark 3 after index) and TlCa₂Ba₃Cu₄O₇ (Mark 4 after index) phases.
Fig. 3 shows the resistivity versus temperature of the films. It indicated an onset of superconductivity at about 140 K and zero resistance at 111 K. It has been predicated that a four-layer Cu–O thallium compound would be superconducting at above 140 K [8]. Both the TlCa₂Ba₃Cu₄O₈ and TlCa₂Ba₂Cu₃O₇ phases observed on the as-grown film showed a broadened transition in the resistivity–temperature curve. The minor phase of TlCa₂Ba₃Cu₄O₈ may be a high-$T_c$ superconducting phase with $T_c$ (onset) above 140 K. However, the major phase of TlCa₂Ba₂Cu₃O₇ leads the $T_c$ (zero) down to 111 K.

In summary, we have successfully synthesized highly preferentially oriented multiple phases of TlCa₂Ba₂Cu₃O₇ and TlCa₂Ba₂Cu₄O₈ by liquid phase epitaxial process. The films were shown to have a superconducting onset temperature at about 140 K and zero resistance at 111 K. The broadened transition of superconductivity, from 140 to 111 K, may be attributed to the co-existence of both TlCa₂Ba₃Cu₄O₈ and TlCa₂Ba₂Cu₃O₇ phases.

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