CVD of Bi-Sr-Ca-Cu-O Thin Films

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ABSTRACT

We developed a chemical vapor deposition (CVD) method for high-Tc superconducting Bi-Sr-Ca-Cu-O thin films, and obtained a high-Tc phase (about 110 K) without postannealing in an atmosphere containing oxygen. Films were deposited on (001) MgO substrates in He in an open-tube reactor with O2 and/or H2O oxidizing agents. The source materials -- anhydrous metal halides such as BiCl3, SrCl2, CaCl2, and CuI -- were evaporated in the CVD system to be used as source gases. The deposition temperature was between 700°C and 850°C. The average deposition rate was about 1.5 nm/min and the average film thickness was about 0.1 μm. Films were a mixture of low-Tc (about 80 K) and high-Tc (about 110 K) phases. Their C-axis orientation was perpendicular to the substrate. Their electrical resistance decreased abruptly below 115 K and the zero-resistance temperature was around 98 K. A critical current density of about 1.7 x 10⁴ A/cm² was obtained at 4.2 K. The O2 in the CVD atmosphere played an important role in determining the phase of films at higher temperature depositions.

INTRODUCTION

Since the high-Tc superconducting material La-Ba-Cu-O was discovered [1], other Perovskite superconducting high-Tc materials have been found. Materials used to fabricate electronic devices must be of high quality -- thin single-crystal films in particular. Many ways have developed to fabricate films, e.g., sputtering, electron beam (EB) evaporation, and molecular beam epitaxy (MBE). We have further developed the chemical vapor deposition (CVD) of Bi-Sr-Ca-Cu-O superconductors, discovered by Maeda et al. [2, 3, 4].

We fabricated high-Tc Bi-Sr-Ca-Cu-O superconductors by CVD without postannealing, and discuss the relationship between film characteristics and deposition conditions in this paper.

EXPERIMENT

Figure 1 diagrams the CVD system, which has four source zones and a deposition zone, each heated by a separate furnace. The source materials -- anhydrous metal halides such as BiCl3, SrCl2, CaCl2, and CuI -- are put in boats placed in the source zones and evaporated by heating. The temperature of each zone is controlled independently so that source gas concentrations can be varied. The source gases are transported to the growth zone by the carrier gas (He). The oxidizing agents, O2 and/or H2O, are transported to the deposition zone separately from the source gases. (001) MgO substrates 30 mm x 30 mm x 0.5 mm are placed in the deposition zone, where the source gases are mixed and react with O2 and/or H2O, and films are deposited on the substrate. The deposition temperature Tsub ranged 700°C to 850°C; typical temperatures of each source zone are shown in Fig. 1. After deposition, the substrates were cooled rapidly at about 30°C/min. The oxygen concentration (COx) ranged from 0.1% to 12.5% of the total gas flow, and the H2O concentration (C02) was between 320 ppm and 3200 ppm. The chemical reaction of H2O in CVD is not understood precisely, but H2O increases the deposition rate. Films were typically about 0.1 μm thick. The films were not annealed in oxygen or an oxygen mixture after deposition. Film characteristics were determined by X-ray diffraction (XRD) using Cu-Kα radiation, and by electrical resistance measurements. We measured film composition by inductively coupled plasma luminescence spectrometry (ICP) and X-ray fluorescence analysis. The composition was Bi: Sr: Ca: Cu = 1:(0.6-1.5):(0.6-1.25):(0.5-3.5). Bumps and segregations in the films prevented the composition estimates from being completely accurate.
RESULTS AND DISCUSSION

Figure 2 shows the electrical resistance of the films versus temperature. The curves are normalized to the resistance at room temperature (300 K). The samples were obtained at $T_{\text{sub}}$=850°C, and at $C_{\text{Ox}}=12.5\%$ for sample 1, 3.75% for sample 2, and 1.25% for sample 3. The resistivity of sample 1 at 300 K is about 1.3 $\mu$m-cm. The resistance of sample 1 decreases from 300 K to 115 K much like a metal, and drops abruptly below 115 K. The zero-resistance temperature is 98 K and the critical current density is $1.7 \times 10^4$ A/cm$^2$ at 4.2 K. The resistivity of sample 2 at 300 K is about 30 $\mu$m-cm, about 20 times larger than that of sample 1. The resistance of sample 2, also much like a metal, decreases abruptly below 90 K, and has a shoulder around 50 K. The zero-resistance temperature is 16 K. There is no change in slope at around 100 K. Thus, the resistance characteristics of this sample do not indicate the existence of a high-$T_c$ phase. The resistivity of sample 3 at 300 K is about 82 $\mu$m-cm, about 60 times larger than that of sample 1. Sample 3 is not superconducting, even at 10 K, but resistance decreases at around 70 K, indicating that this film has a superconducting phase. As these samples show, the superconductivity and high $T_c$ of the films depends on the oxygen concentration during deposition. This concentration plays an important role in deposition at 850°C. Samples 4 and 5 (Fig. 3) were deposited at 700 K. The oxygen concentrations in the atmosphere were 12.5% for sample 4 and 1.25% for sample 5. The resistivity of sample 4 was 1.3 $\mu$m-cm and that of sample 5 was 0.85 $\mu$m-cm. The resistance of these samples starts to decrease around 100 K, and drops abruptly at about 90 K. Sample 4 has a shoulder around 100 K. The zero-resistance temperature of samples 4 and 5 is around 77 K. These results show that the oxygen concentration dependence is less in low-temperature than in high-temperature deposition.

Figures 4 and 5 show the X-ray diffraction patterns of the films. In all samples, the C-axis is perpendicular to the surface of the MgO substrate. The X-ray diffraction pattern for sample 1 shows two main kinds of peaks related to the C-axis of the high- and low-$T_c$ phases. This indicates that the film was a mixture of phases, even though this sample is superconducting at 98 K, and that the film has high-$T_c$ phase paths. The pattern for sample 2 shows that the film has only a low-$T_c$ phase. Sample 3 also has a low-$T_c$ phase, but is not superconducting. The resistance characteristics of sample 3 shows that it is a mixture of low-$T_c$ and...