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Electrical and Structural Properties of Ex-situ Annealed Superconducting $Bi_2Sr_2CaCu_2O_8$ Thin Films Obtained by Coevaporation of Components

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Abstract

$Bi_2Sr_2CaCu_2O_8$ system superconducting thin films were obtained by synchronized deposition of Bi, Cu, CaF_2 and SrF_2 components onto cleaved MgO (100) single crystal substrates after annealing in the temperature range 600–840 °C. The films were annealed in H_2O and O_2, then dry O_2 atmosphere for the removal of fluorine from the structure and to attain superconducting properties. X-ray powder diffraction patterns were used to characterize the obtained film structure. The films were observed to grow along c-axis perpendicular to the substrate surface with the identified reflection on the ($00l$, l = 6, 8, 10 ...) planes. The films having the critical temperature higher than liquid nitrogen were obtained when Bi and the other components were evaporated from separate sources. DC resistance in the films were measured in the temperature range 77–300 K. of those films having good superconducting properties, metallic behaviors were seen in the normal state and zero resistance at 79 K was obtained following a transition in the resistance.

Key Words: Superconductivity, BSCCO, 2212 phase, thin film, coevaporation, ex-situ annealing.

1. Introduction

Bi-based superconductor compounds of the form $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, where $n = 1, 2, 3$ gives the number of CuO_2 layers, have been studied extensively by many groups. In this material, known superconducting phases are the (2201), (2212) and (2223) phases, for $n = 1, 2, 3$, with the critical temperatures of 10–20 K, 60–85 K and 110 K, respectively [1]. According to previous studies, the $n = 2$ phase was found more stable and more easily obtained than the (2223) phase. The phase associated with $n = 3$, $Bi_2Sr_2Ca_2Cu_3O_{10}$, can be obtained in stable form by doping the structure with a small amount of Pb. The Pb atoms are thought to reside at the Bi sites in the structure, giving rise to the composition formula $Bi_{2-x}Pb_xSr_2Ca_{n-1}Cu_nO_{10+y}$. Optimum amount of Pb is about 15% which gives $x = 0.3$ [2].

RF sputtering techniques, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), chemical vapor deposition (CVD) and metal organic chemical vapor deposition (MOCVD) methods have been intensively employed to obtain superconducting thin films of BSCCO. Films were usually prepared on heated single crystal substrates with oxidation performed in-situ, requiring relatively complicated and expensive systems. A BSCCO target or a stoichiometric BSCCO crystal is also necessary as the starting material. Thermal

evaporation techniques were also used to prepare thin films of BSCCO and other high Tc superconducting materials [3]. Methods of flash evaporation and electron beam evaporation have also been employed. All above-mentioned methods require the starting materials be in stoichiometric proportions. Due to the difficulty of developing the superconducting phase in fresh made films, ex-situ annealing was found necessary for may cases.

Evaporation of the components onto heated crystal substrates in reactive atmosphere has also been carried out as an alternative method. Due to the difficulty of the controlling the various process-sensitive parameters, including the insertion of the reactive gases into the vacuum chamber, a two-step preparation process may be preferred. In the first step, precursors are evaporated onto the crystal substrate. In the second step, precursors on the substrate are annealed at high temperature in a convenient atmosphere. This method is known as an ex-situ preparation of the HTS materials. Ex situ techniques have been successfully applied in the preparation of BSCCO (2223) ultra thin films [4], YBCO (123) thin [5] and thick films [6]. In previous works we have studied ex-situ annealing of YBCO (123) [7] and BPSCCO (2223) [8] thick films prepared by screen printing on various kinds of substrates.

In the present work, we have employed the ex-situ method to prepare the (2212) phase of Bi-based superconductor thin films.

2. Film Deposition, Annealing and Characterization

Much experience has come to show that, due to bismuth's low melting point and high vapor pressure, films with the best properties are achieved by evaporating the Bi component physically separate from the other components. It is also observed that Cu in the structure can be put in metallic form. Due to the difficulty of evaporating Sr and Ca in metallic, oxide and carbonate forms, their fluorides have been preferred.

Thus in this work, film deposition was carried out under high vacuum by evaporating the compound components using a pair of resistively heated tungsten sources. One source was used to evaporate metallic Bi, while the second source, operated simultaneously, evaporated Cu, SrF_2, and CaF_2 components. The evaporation sources were typically separated from the substrates by a distance of about 6 cm. All components were weighed out and used in stoichiometric ratios. Evaporation occurred under 1–2 $\times$ 10^{-6} torr onto unheated substrates.

Following evaporation, films were annealed for 30 minutes in the temperature range 700–840 °C in an H_2O + O_2 atmosphere, to aid the removal of fluorine from the structure and to develop superconducting properties. Crystal structure and removal of fluorine is associated with the following chemical reaction:

$$[Bi + Cu + SrF_2 + CaF_2] \text{ (precursors)} \ + H_2O + O_2 \rightarrow Bi_2Sr_2CaCu_2O_8 + HF(g) \qquad (1)$$

The films were then annealed in dry O_2 atmphosphere for 6 hours at 600 °C.

The method of x-ray powder diffraction (XRD), with Cu-K_α radiation, is used to characterize the obtained films. A typical example of the XRD pattern is shown in Figure 1, which shows the intensity of the peaks as a function of 2θ. In the figure, in addition to the MgO (100) substrate, the fundamental reflections for the $(00l)$, l = 6, 8, 10... planes are seen clearly as evidence for the preferred orientation being parallel to the substrate surface. Some unidentified reflections with small intensities were also observed in the reflection patterns. These reflections may arise due to the existence of impurities, such as unreacted Bi, Cu and others. We found the c axis length of the unit cell as $c = 30.75$ Å computed from the reflection patterns. This result is in good agreement with published results [9].

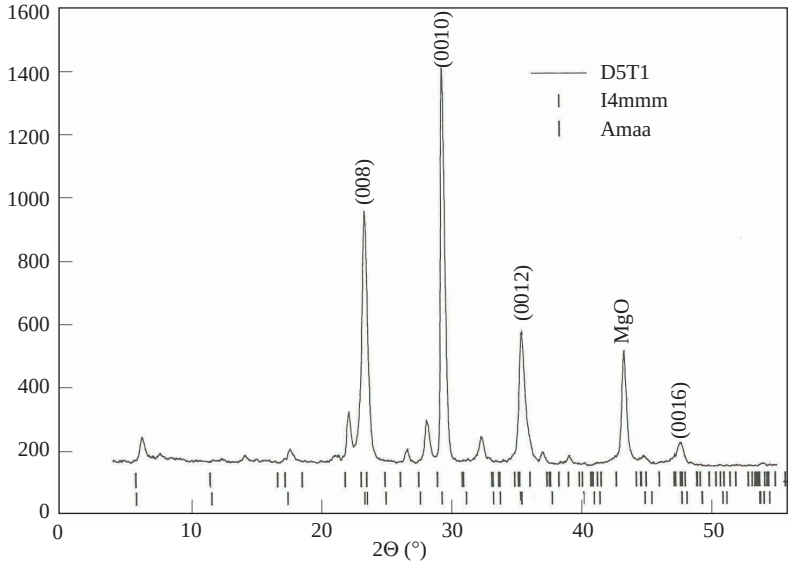

Figure 1. XRD pattern of a thin film on MgO (100) substrate. Small reflections due to impurities were also seen in the pattern.

3. Results and Discussions

Electrical contacts were created by evaporating thin strips of Ag in high vacuum onto the thin films. Dc resistance was characterized by four-point probe technique in the temperature range 300–77 K. A constant current source is attached to the outer contacts with a 10 μA agitating current, while the voltage drop between the inner contacts were measured via a nanovoltmeter. At every measurement point, temperature of the sample was kept constant and voltage measurements were repeated by reversing the current direction to eliminate the possible contribution of thermoelectric voltages. Temperature and the other parameters were controlled and measured under computer control. Good samples showed metallic behavior from room temperature down to onset temperature. Onset temperatures for 2212 structures were seen in the 85–90 K range. In general, we obtained the zero resistance below the temperature of liquid nitrogen. The best film we prepared exhibited the resistance-temperature variation shown in Figure 2. Zero resistance was seen at 79 K for this sample.

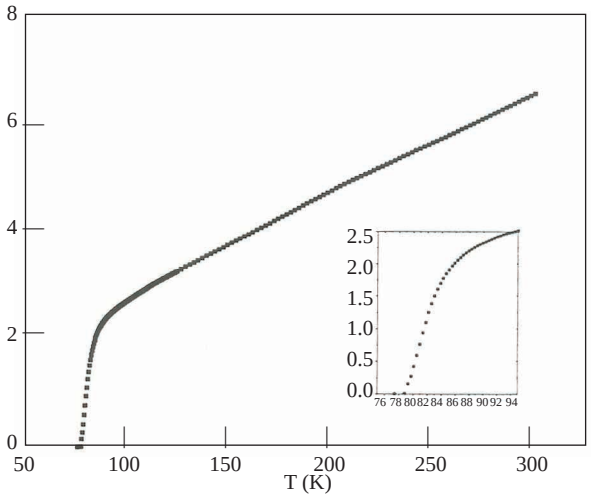

Figure 2. Temperature dependence of the dc resistance of a thin film. Insert shows the transition region in detail.

4. Conclusion

We have shown superconducting thin films of BSCCO can be prepared in the (2212) phase by ex-situ annealing. The composite films were deposited onto unheated MgO (100) substrates using co-evaporated components in metallic and fluoride form, evaporating the starting materials of Bi, Cu, SrF_2 and CaF_2 in high vacuum in a single, unified step. A high temperature annealing in water vapor and oxygen atmosphere was found necessary for the removal of fluorides, formation of the crystal structure and to attain the superconducting properties.

This method overcomes the difficulty of handling and evaporating Sr and Ca metals, metal oxides and carbonates but introduces another difficulty: the removal of fluorides in the water vapor atmosphere. This difficulty can be over come by ex-situ annealing.

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