Materials Chemistry and Physics 216 (2018) 153–157

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

High efficiency preparation of $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconducting thin films by an acetate based Sol-Gel process

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HIGHLIGHTS

- A high-efficiency and environmentally friendly acetate based sol-gel method for Bi-2212 films is proposed.
- The whole heat treatment process only needed 4 h, which is good for environment protection and energy conservation.
- The prepared Bi-2212 superconducting films exhibit good growth textures and excellent superconductivity.

ARTICLE INFO

Keywords:
Bi-2212
Sol-Gel
Microstructure
Oxygen partial pressure
Superconductivity

ABSTRACT

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconducting thin films with *c*-axis epitaxial orientation were prepared on $LaAlO_3$ (LAO) single crystal substrates via a Sol-Gel technique using metallic acetates as starting materials. The influence of the growth temperature and oxygen partial pressure (pO_2) on the phase purity and superconducting properties of Bi-2212 was discussed. The results show that Bi-2212 films prepared at 820 °C with the pO_2 of 1.4 KPa exhibit good in-plane and out-of-plane growth textures and excellent superconducting properties with high critical transition temperature (T_c) of 88 K and narrow transition width (ΔT_c) of 4.8 K.

1. Introduction

Since the discovery of $Bi_2Sr_2Ca_nCu_{n+1}O_\delta$ (BSCCO), it has been researched extensively, due to its good properties, for improving its superconductivity and structure property. Therefore, BSCCO is found to be a potential candidate for superconducting wires [1], superconducting tapes [2] and microelectronic devices [3]. In addition, BSCCO superconducting thin films have been expected to realize the application of THz technology due to its intrinsic Josephson effect [4]. In Bi-based superconductor system: Bi-2201 phase with Tc of ~24 K, Bi-2212 phase with Tc between 80 K and 96 K and Bi-2223 phase with Tc of ~110 K. Besides a good superconductivity, Bi-2212 is much more thermodynamically stable over a wide temperature than Bi-2223 phase [5]. As a consequence, Bi-2212 has attracted considerable attention for a long time. So far, Bi-2212 thin films have been prepared on single crystal substrates, Ag substrates, or MgO substrates by Pulsed Laser Deposition [6], Mechanical Exfoliation [7], Microwave Techniques [8] or Molecular Beam Epitaxy [9]. In some cases, Bi-2212 superconducting films can be produced directly from Bi-2212 powders in pure oxygen or vacuum condition [10–12]. Pb-doped Bi-2212 phase can not only lower the heat-treatment temperature but also shorten the heat-treatment time, however, it is toxic and unfriendly to environment [13,14].

Therefore, a simple and eco-friendly method for preparing Bi-2212 thin films is urgently needed. Compared with other techniques, Sol-Gel technique has many advantages such as low cost, high efficiency, easy handling, molecular level homogeneity, environment protection and energy conservation [15-18]. So far, there are only a few reports about BSCCO superconductors prepared by Sol-Gel technique. And most of the researchers chose alkoxides or nitrates as starting materials [19–21]. As we known, alkoxides are expensive, and nitrates usually release NH_3 and NO_2 that destroy the surface quality of Bi-2212 films during the heat treatment process [22].

To avoid these problems mentioned above, *c*-axis epitaxial Bi-2212 films were prepared on $LaAlO_3$ (LAO) substrates by Sol-Gel method using Bi-acetate, Sr-acetate, Ca-acetate and Cu-acetate as starting materials. LAO (3.8 Å) and Bi-2212 (5.4 Å) has a small lattice mismatch of 0.49% in 45-degree rotated lattice matching relation in a-b plane, it is good for improving film growth and film quality. The effects of heat-treatment temperature and oxygen partial pressure on the quality of Bi-2212 films were investigated in detail to improve their phase purity and

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https://doi.org/10.1016/j.matchemphys.2018.06.007
Received 20 September 2017; Accepted 3 June 2018
Available online 04 June 2018
0254-0584/

superconductivity. After optimizing heat treatment parameters, the whole heat-treatment time was shortened to 4 h.

2. Experimental procedure

2.1. Preparation of Bi-2212 films

Analytical reagent $Bi(CH_3COO)_3$((Bi)Ac3), $Sr(CH_3COO)_2{\cdot}1/2H_2O$(Sr(Ac)2), $Ca(CH_3COO)_2{\cdot}H_2O$($Ca(Ac)_2$) and $Cu(CH_3COO)_2{\cdot}H_2O$($Cu(Ac)_2$), acrylic acid (AA) and methanol (MeOH) were used as starting material, chemical modifier and solvent to synthesize Bi-2212 solution. Fig. 1 shows the process for the preparation of Bi-2212 solution. $(Bi)Ac_3$, $Sr(Ac)_2$, $Ca(Ac)_2$ and $Cu(Ac)_2$ were dissolved into AA and MeOH respectively in a stoichiometric quantity of $(Bi)Ac_3$:AA:MeOH = 1:10:20, $Sr(Ac)_2$:AA:MeOH = 1:12:20, $Ca(Ac)_2$:AA:MeOH = 1:12:20 and $Cu(Ac)_2$:AA:MeOH = 1:3:60 at room temperature to prepare Bi-solution, Sr-solution, Ca-solution and Cu-solution, respectively. Then the four solutions were mixed in the controlled stoichiometry of Bi:Sr:Ca:Cu = 2:2:1:2, stirred and aged for 48 h to form the stable Bi-2212 solution.

In order to investigate the effect of heat treatment temperature on phase purity of Bi-2212, four groups of Bi-2212 gel films were prepared on LAO substrates by dip-coating method and heat treated at 780 °C, 800 °C, 820 °C and 840 °C, respectively. Fig. 2 shows the heat treatment profile of Bi-2212 films. During the heat-treatment process, Bi-2212 gel films were firstly heated up to 420 °C from room temperature in humid N_2, it is aim to exhaust air and avoid film toughing and drying. Subsequently, Bi-2212 films were heated up to 600 °C in dry O_2, and the content of O_2 should be enough to form the intermediate phase completely at this stage. Then the Bi-2212 films were heated up to 780 °C, 800 °C, 820 °C or 840 °C and crystallized for 40 min in humid N_2 mixed with small amounts of O_2. Oxygen content has an important effect on the phase formation of Bi-2212 during high-temperature phase formation process, and it will be discussed in detail in 3.2. Finally the Bi-2212 films were dwelled at 550 °C for 50 min in dry O_2 to fill oxygen vacancies [23]. The whole heat treatment process only needed 4 h and the high-temperature phase formation process only needed 40 min.

2.2. Characterization

A SmartLab X-ray diffractometerin θ-2θ, ω and φ scan modes (XRD) is used to determine the phases, the out-of-plane texture, and the in-plane texture, respectively. Scanning electron microscopy (SEM) experiments are conducted on a JEM-6700F and energy dispersive spectrometry (EDS) was adopted to detect the composition of the films. Curves depicting the resistance–temperature (R–T) characteristics of the films were measured by A VersaLab multi-function vibrating sample magnetometer (VSM).

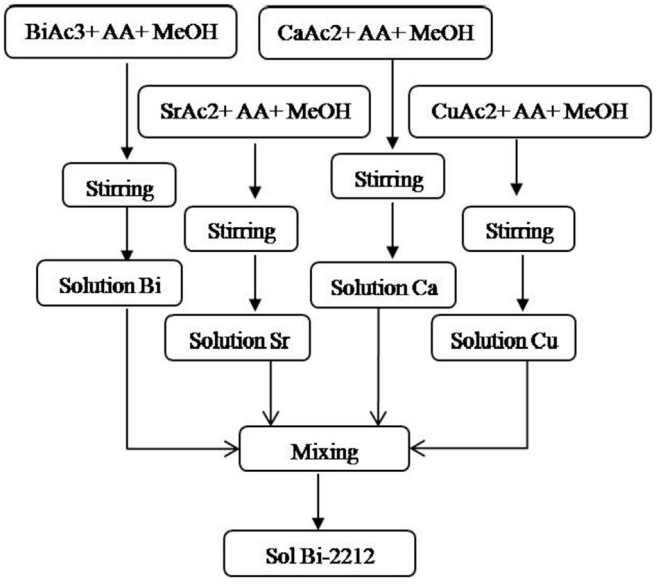

Fig. 1. Flowchart for the preparation of Bi-2212 Solution.

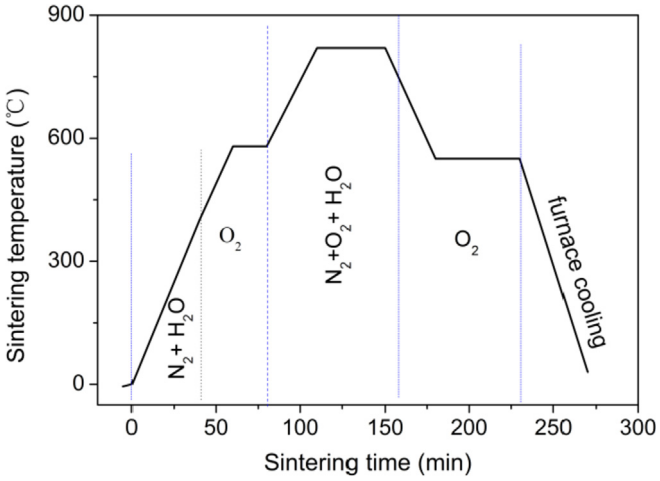

Fig. 2. Profile for the heat treatment of Bi-2212 thin films.

3. Results and discussion

3.1. The effect of heat treatment temperature on phase purity of Bi-2212

Fig. 3 shows XRD patterns of the Bi-2212 films heat-treated at 600 °C. As seen, Bi_2O_3, SrO, CaO, CuO, $CaSrCuO_3$ and $Bi_2Sr_3Cu_2O_8$ were detected, indicating that the acetates have been decomposed to form the above oxides and then the oxides interreacted with each other to yield some other intermediate products at 600 °C. The related chemical reactions are represented in equations (1)–(6).

$$2Bi\ (CH_3COO)_3 + 12O_2 \rightarrow Bi_2O_3 + 12CO_2\uparrow + 9H_2O \quad (1)$$

$$Sr(CH_3COO)_2 + 4O_2 \rightarrow SrO + 4CO_2\uparrow + 3H_2O \quad (2)$$

$$Ca(CH_3COO)_2 + 4O_2 \rightarrow CaO + 4CO_2\uparrow + 3H_2O \quad (3)$$

$$Cu(CH_3COO)_2 + 4O_2 \rightarrow CuO + 4CO_2\uparrow + 3H_2O \quad (4)$$

$$SrO + CaO + CuO \rightarrow CaSrCuO_3 \quad (5)$$

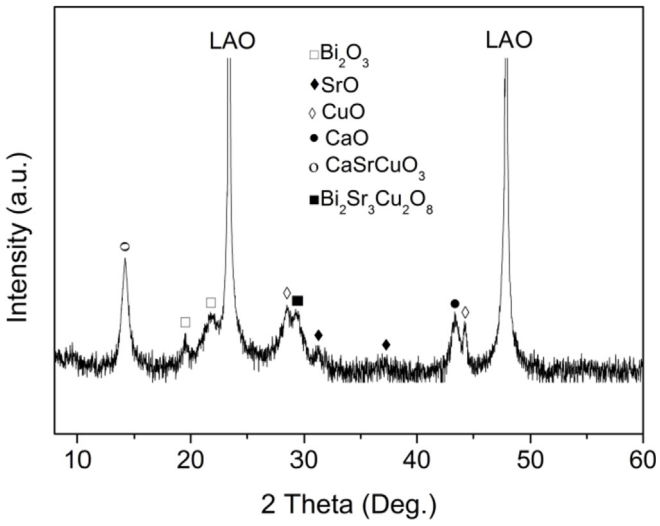

Fig. 3. XRD patterns of Bi-2212films heat-treated at 600 °C.