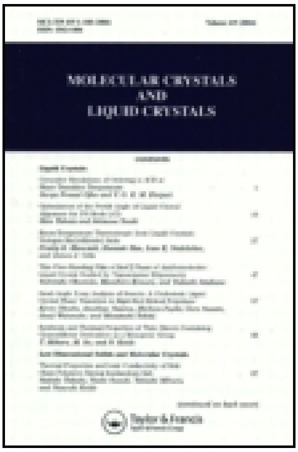

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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$Bi_2Sr_2CaCu_2O_y$ Ultra-Thin Films Prepared by Metallo-Organic Deposition Method

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$Bi_2Sr_2CaCu_2O_y$ ULTRA-THIN FILMS PREPARED BY METALLO-ORGANIC DEPOSITION METHOD

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Abstract

Metallo-organic deposition is a non-vacuum technique for thin film fabrication which allows easy alteration of chemical components and no requirement of an expensive system. We report the preparation of ultra-thin film superconductors which are almost transparent with homogeneous surfaces by this method using carboxyrates solutions. By a careful pyrolysis and rapid thermal annealing technique, pure $Bi_2Sr_2CaCu_2O_y$ superconductors with c-axis strongly aligned perpendicular to the substrate surface were attained.

INTRODUCTION

Thin film preparation techniques are mainly classified to two methods. One is a vacuum deposition technique such as thermal evaporation, sputtering, electron or laser beam evaporation, chemical vapor deposition(CVD), and molecular beam epitaxy(MBE). The other is a non-vacuum deposition technique such as metallo-organic deposition(MOD) via spin-coating or dip-coating using solution precursors, and a sol-gel method. The later is a promising method because of the wide variety of in choice materials, no requirement of expensive instruments, forming films over large areas with complicated shapes, and mixing each component in a molecular scale.

The disadvantage of the method in general is that the film depostion and the synthesis of superconducting phase can not be performed at the same time. For $YBa_2Cu_3O_y$(YBCO) superconducting films, the epitaxial growth was achieved on $SrTiO_3$[100] substrates, indicating that the film deposition and formation of the superconducting phase were made simultaneously.[1,2,3,4,5] For the Bi-system superconducting films, however the epitaxial growth has been reported in only a few papers.[6] At this stage, the MOD has the possibility to form identical quality of thin films to the vacuum deposition technique. For some applications, it is essential for materials to have critical current densities(J_c) in excess of $1x10^5 A/cm^2$, however the J_c of the materials derived from these methods is lower than that from the vacuum techniques.

The first step to increase the J_c by MOD is to prepare high quality films with morphology comparable to that by the vacuum techniques. Recent experiments [7,8,9] have shown that rapid thermal annealing(RTA) of YBCO films, which were deposited by electron beam deposition and MOD, enable us to produce thin film superconductors having sharp superconducting transitions, and it was further found that the epitaxial grain growth on the $SrTiO_3$ surface was achieved by the RTA.

In this paper, we describe the optimization of the MOD process to prepare $Bi_2Sr_2CaCu_2O_y$(2212) superconducting thin films using naphthenates, 2-ethylhexanoates(2EH), and caprylates precursors. X-ray diffraction analysis(XRD) shows superconducting thin films with the thickness of 0.3μm are completely c-axis oriented to the MgO[100] surface. Improvement in superconducting properties of the samples with the RTA treatment suggests that the enhancement of grain contacts occurred by grain growth.

EXPERIMENTAL

Naphthenates, 2EH, and caprylates precursors were prepared by dissolving each carboxylate in toluene with the cation ratio of Bi:Sr:Ca:Cu=2:2:1:2. In the case of 2EH and caprylates precursors, chloroform was added to dissolve Cu-salts perfectly which have low solubility to toluene. The concentration of total metals for each precursor was adjusted to be approximately 4wt.%. Viscosity of the precursors was 2.30, 0.44, and 0.50poise, respectively. Differential thermal analysis(DTA) and thermogravimetric analysis(TG) were performed at a heating rate of 5°C/min in nitrogen and oxygen atmospheres. Specimens were vacuum dried before the analysis to expell volatile solvent. The precursor solution was spin-coated on a single crystal MgO[100] substrates($10x10x1mm^3$) at 2000-4000rpm which resulted in formation of a smooth as-coated film surface. The number of dropping times was changed 3-10 to get the final film weight of 100-200μg. Coated films were dried at 100°C in a vacuum oven, pyrolized in N_2 by heating, at a rate of 2°C/min, to 600°C, then flashed air to complete the pyrolysis process. Pyrolized films were fired in air at a constant temperature, and also processed by the RTA in air. The RTA was achieved using a gold furnace at a heating rate of 30°C/min above 800°C. The films were rapidly cooled by taking out to the ambient atmosphere. The thickness of the films was measured by optical surface roughness analizer, DEKTAK, and observation of fractured the surface using scanning electrom microscopy(SEM). The specimens were characterized by XRD, a. c. susceptibility, optical microscopy, electron probe microanalysis(EPMA), and d. c. resistivity measurement by a standard four probe method using indium soldier contacts.

RESULTS AND DISCUSSION

Figure 1 shows the TG the and differential TG(DTG) curves of precursors of naphthenates, 2EH, and caprylates examined in N_2 flow. Three major decomposition steps were recognized for these precursors. The first DTG peaks around 250°C are mainly due to decomposition of Cu-salts, second peaks at 300°C are caused by decomposition of Bi-salts, and the last over 400°C are attributed to the decomposition of Sr- and Ca-salts. No substantial difference in the decomposition behaviors was detected, however the separation of DTG peaks of Cu- and Bi-salts is apparent for naphthenates, and obscure for caprylates. Main weight loss was observed in the temperature range from 200 to 350°C. Accordingly, a carefull pyrolysis process is required in this temperature range. Decomposition of carboxylates in inert atmosphere is endothermic, but substantial exothermic heat was liberated in the DTA analysis under oxygen flow. This suggests that gas products yielded by the decomposition such as carbon monoxide and hydrocarbon[10] react with O_2 to increase the specimen temperature. Optical observations of the coated films using a gold furnace showed occurrence of bloating between 200 and 300°C in air. Accordingly a carefull pyrolysis process in inert atmosphere seems to be necessary for preventing the films from bloating. Figure 2 shows the XRD patterns of the films derived from a caprylate precursor with the thickness of approximate 0.3μm fired at 825, 830, and 835°C for 15 mins in air. Stronger diffraction peaks corresponding to (00n) of the 2212 phase are shown for the films fired at lower temperature. The films fired at 840-860°C have another impurity peaks assigned to be (00n) of the $Bi_2Sr_2CuO_y$(2201) phase. Temperature above 820°C is necessary to form the 2212 phase, while fillms the fired below the temperature were composed of the mixture of BiO_3, CuO, $SrCO_3$, and $CaCO_3$. It should be noted that the films fired below 830°C have smooth surfaces with gray color and almost transparent, however, those fired above 830°C have rough and non-uniform surfaces. Scanning electron micrographs of the films fired at 825 and 835°C are shown in Figure 3. The film fired at 825°C contains plate-like small grains of the 2212 phase. Larger needle-like grains and small spherical grains were observed in the films fired at 835°C. The temperature around 830°C is critical to obtain uniform morphology of the film surface. EPMA results showed these needle-like grains are constituted by the $(Sr,Ca)_3Cu_5O_y$. Considering the XRD results, the 2212 phase decomposes to yield the 2201 phase and the $(Sr,Ca)_3Cu_5O_y$ at higher firing temperatures. In the case of another precursors, definite difference was not observed in the XRD patterns or in SEM. Increasing firing duration does not change the XRD patterns, however, crystallography of the film surface tends to be smoother. The film fired at 825°C for 15hrs has square-shaped plate-like grains with the length of 2-3μm, indicating the existence of partially epitaxial-grown grains. Figure 4 shows the temperature dependence of a.c. susceptibility for the film fired at 825°C for 4hrs. A definite amount of decrease in susceptibility was detected below 76K for the film of the thickness of about 0.3μm, almost identical to the penetration depth of this superconductor. The film fired for 15 mins did not show any susceptibility change, suggesting that a long time firing improves superconducting properties. Temperature dependence of resistivity of the film fired at 825°C for 1hr is shown in Figure 5 (a). Large amount of resistivity drop was observed but zero resistivity was not achieved. The result indicates that grains of the film constituted by the pure 2212 phase, which was confirmed by XRD, were not coupled well each other. In Figure 5 (b), temperature dependence of resistivity of the film, which was rapidly heated in one minute from 810 to 850°C and then kept at 825°C for 1hr, is shown. This figure shows the RTA treatment is effective to improve the superconducting property. In the optimized RTA treatment, sudden occurrence of partial melting enhances grain growth to strengthen the grain coupling and the treatment is short enough not to decompose 2212 phase to 2201 phase and $(Sr,Ca)_3Cu_5O_y$.

In summery, uniform and pure $Bi_2Sr_2CaCu_2O_y$ superconducting thin films of 0.3μm thickness were produced by MOD in which were carefully controlled during the pyrolizing and firing stages . The films were strongly c-axis aligned perpendicular to the MgO substrate surface. Tailing of the resistivity was eliminated by adopting RTA.

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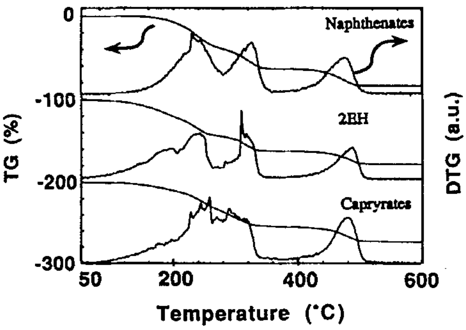

Figure 1 TG and DTG curves of naphthenates, 2EH, and caprylates precursors.

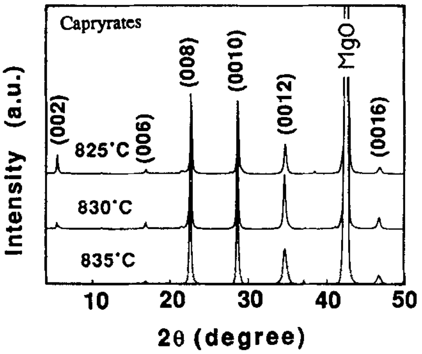

Figure 2 XRD patterns of the films using caprylates precursor fired at 825, 830, and 835°C.

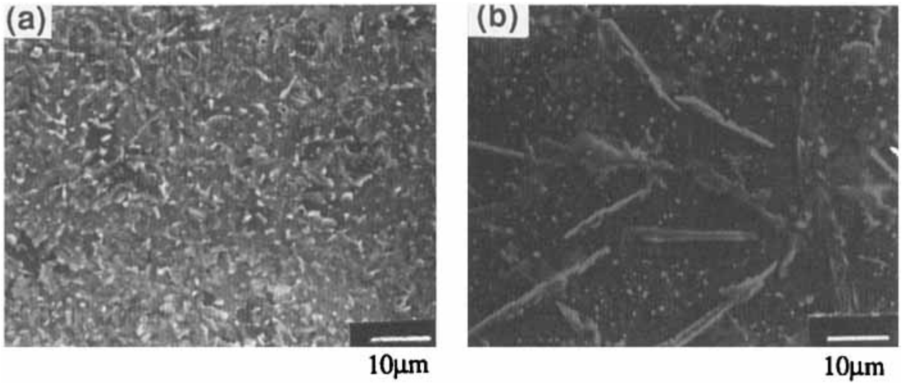

Figure 3 Scanning electron micrographs of the films fired at ; (a) 825°C and (b) 835°C .

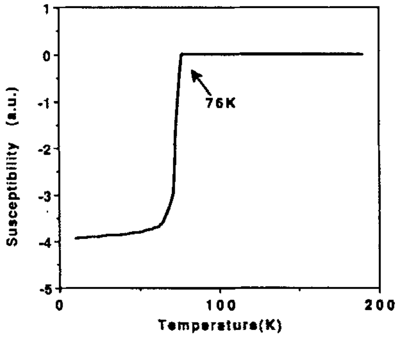

Figure 4 Temperature dependence of magnetic susceptibility of the film fired at 825°C for 4hrs.

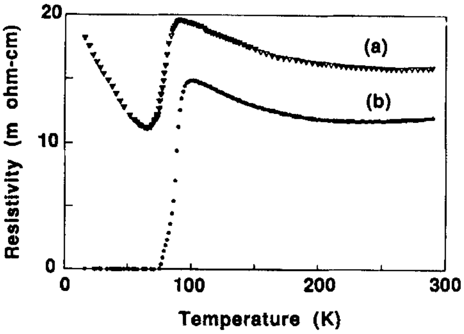

Figure 5 Temperature dependence of resistivity of the films : (a) fired at 825°C ; (b) treated by RTA[850-825°C].