Production and Characterization of BalrO₃ Doped Superconducting YBCO Thin Films by TFA-MOD Method

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Abstract

Key words Superconductivity, Thin film, YBCO, TFA-MOD, BalrO₃ BalrO₃ (BIO) doped YBa₂Cu₃O_{7- δ} (YBCO) superconducting thin films were prepared using yttrium, barium and copper acetate on SrTiO₃ (STO) single crystal substrates by Trifluoroacetic Acid-Metal Organic Deposition (TFA-MOD) method. The effect of added BIO nanoparticles on the film structure and superconducting properties were studied. Highly textured YBCO superconducting thin films on STO substrate were deposited by spin coating technique. Surface morphologies of the films were observed by Scanning Electron Microscopy (SEM) and the morphological quality of the thin films was determined through atomic force microscopy (AFM). The phase analyses of the films were investigated by X-Ray Diffractometer (XRD). In order to determine superconducting properties critical transition temperature (T_c) values of films were measured by using standart four point method. All YBCO films with BIO nanoparticles had T_c values over 91K. Results indicate that BIO added YBCO films exhibit denser surface and higher T_c values than undoped YBCO films.

BalrO₃ Katkılı Süperiletken YBCO İnce Filmlerin TFA-MOD Yöntemi ile Üretilmesi ve Karakterizasyonu

Özet

Anahtar kelimeler Süperiletkenlik, İnce film, YBCO, TFA-MOD, BalrO₃. BalrO₃ (BIO) katkılı YBa₂Cu₃O₇₋₆ (YBCO) süperiletken ince filmler, yitrium, baryum ve bakır asetatlar kullanılarak SrTiO₃ (STO) tek kristal altlıklar üzerine Trifluoroasetik Asit-Metal Organik Depozitleme (TFA-MOD) yöntemi kullanılarak hazırlanmıştır. BIO nanopartikül katkıların film yapısı ve süperiletkenlik özelliklerine olan etkileri araştırılmıştır. Yüksek oranda tekstürlenmiş YBCO süperiletken filmler STO altlıklar üzerine spin kaplama yöntemi kullanılarak kaplanmıştır. Filmlerin yüzey topgrafyaları taramalı elektron mikroskobu (SEM) ile, yüzey kaliteleri ise atomik güç mikroskobu (AFM) vasıtasıyla belirlenmiştir. Üretilen filmlerin faz analizleri X-Ray difraktometresi (XRD) kullanılarak araştırılmıştır. Süperiletkenlik özelliklerden kritik geçiş sıcaklığını (T_c) ölçmek için standart dört nokta yöntemi kullanılmıştır. BIO katkılı YBCO filmlerin tümünde 91K ve üzerinde geçiş sıcaklığı değerleri elde edilmiştir. Elde edilen sonuçlar incelendiğinde BIO katkılı YBCO filmlerin katkısız YBCO filmlere göre hem daha yoğun bir yüzeye hem de daha yüksek T_c değerlerine sahip oldukları gözlemlenmiştir.

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1. Introduction

Trifluoroacetic acid metal organic deposition (TFA-MOD) method is a most attractive technique to fabricate high quality superconducting thin films because of the high production rate and the possibility of low cost (Inoue *et.al.*, 2009). YBa₂Cu₃O_{7- δ} (YBCO) is the most promising high temperature superconductors due to its high

potential for some practical applications which include energy storage systems, current limiters, magnetic bearings etc., above liquid nitrogen temperature (77K). For these applications, it requires high value of critical current density (J_c) even at higher applied magnetic fields. To increase J_c of YBCO superconducting thin films at high magnetic fields flux pinning properties of thin films has to be increased (Pomar *et.al.,* 2007). High temperature superconductors have short coherence length therefore nanosized precipitates are necessary to increase effective pinning sides. BalrO₃, BaHfO₃, Y₂BaCuO₅, BaZrO₃ and Y₂O etc. can be used as a nanosized precipitates to create artificial pinning centers (Engel *et.al.*, 2007).

Recently, many research groups studied BZO added YBCO thin films by using TFA-MOD method (Strickland *et.al.*, 2008). However, no results are published about BalrO₃ (BIO) doped thin films which are fabricated by chemical method. Therefore, in this study, BIO doped YBCO superconducting thin films were prepared using yttrium, barium and copper acetate on SrTiO₃ (STO) single crystal substrates TFA-MOD method. The effect of added nanoparticles on the film structure and superconducting properties were studied.

2. Material and Method

The precursor solutions of YBCO were prepared by dissolving acetates of Y, Ba and Cu into distilled water in a 1:2:3 cation ratio with arbitrary quantity of trifluoroacetic acid (TFA) at room temperature (10 ml TFA for 25 ml final solutions). This aqueous solution was refined under vacuum atmosphere with evaporator in order to remove the solvent and to yield a glassy blue residue containing impurities of water and acetic acid. The residue was dissolved in sufficient methanol and refined again to expel the impurities to yield a glassy blue residue containing methanol. The concentration of the solution was fixed to 0.25M with addition of methanol with a certain ratio. The final solution was divided into four parts and different amounts of iridium were added to each part by dissolving Ir (III) pentanedionate in the solutions. The Ir concentrations were adjusted to 0, 1, 3 and 5 mole%. Solution preparation process was adapted from the study executed by Birlik et.al. (2010) with BaZrO₃ particles in the YBCO film structure. The precursor solution was coated by using a spin coater on SrTiO₃ (100) single crystal substrates with a spin rate 6000 rpm for 60 s. The atmosphere

controlled heat treatment system used in this study (Total gas flow 2 liter/minute, -25°C dewpoint for dry gas and 18°C dewpoint for humidified gas flow). The heat treatment recipe was adapted from the study which promoted by Obradors et.al. (2004) and Birlik et.al. (2010). They produced thin films which have a smooth, crack free surface and c-axis oriented grains. According to this recipe, dry gas treatment up 60°C prevents the gel film from absorbing humidity that would deteriorate film integrity. After that the furnace was heated slowly to 390°C in humidified flowing oxygen to suppress the sublimation of Cu trifluoroacetate. During pyrolysis step metal trifluoroacetates decompose and harmful gaseous residues are removed. After that, the furnace was heated up to 780°C for the crystallization under humidified N_2 with 1000 ppm O_2 . The final superconducting films were obtained after oxygenated at 450°C.

X-ray diffraction (XRD) (Rigaku D/MAX-2200/PC) was used to identify crystalline phases. The surface topographies and morphologies of YBCO films were determined by using scanning electron microscope (SEM) (JEOL JSM 6060). The morphological quality of the thin films was determined with the help of atomic force microscopy (AFM) (Nanosurf Easyscan II). Critical temperature of YBCO thin films were determined by using standard four probe technique (JANIS SHI-4 Series 4.2K Cryostat).

3. Results and Discussion

The θ -2 θ diffraction patterns (Cu K_{α} radiation) of undoped and BIO doped YBCO films are shown in Figure 1. It was found that undoped and BIO doped films show strong YBCO peaks on STO substrates.



Figure 1. X-ray θ -2 θ scans of samples including undoped and BalrO₃ doped YBCO with a Cu K α radiation.

The major peaks are (001) and (100) reflections of YBCO phase and STO substrate respectively. This behavior is quite likely to be a key feature for development of YBCO based superconducting films. These results also indicate that the YBCO films have c-axis texture and this signifies to be a superconducting phase. Note that in this case that an additional BalrO₃ (002) phase is present in the Ir doped YBCO samples. Araki, Yamagiwa & Hirabayashi (2001) have fabricated undoped YBCO thin films on STO substrate by similar method and obtained the same XRD patterns.

The surface morphology of undoped and BIO doped YBCO thin films on STO substrates are presented in Figure 2. All films have smooth and crack free surface. It should be noted that they generally have c-axis oriented grains, whilst their surface morphologies different from each other. Needle-like particulates represent a- or b-axis oriented YBCO grains (Rufoloni et.al., 2006). It is very important that these films generally have c-axis oriented for superconducting properties. As it can be seen from SEM pictures, undoped and 1 mole% doped YBCO films have some needleshaped crystal structures, but for 3 and 5 mole% BIO doped YBCO films these needle-shaped particulates disappeared. Note that BIO doped YBCO films have small grain size compared with the undoped YBCO films. The surface morphologies of YBCO based samples are additionally characterized

by means of AFM in order to determine surface roughness values of superconducting thin films. Figure 3 depicts 63.2 x 63.2 μ m AFM 2D images of the surface of undoped and 3 mole% Ir added YBCO thin films on STO substrates. The average surface roughness (S_a) were 5.23 nm and 6.73 nm of pure and 3 mole% Ir doped YBCO films respectively.



Figure 2. SEM micrographs of pure and BIO added YBCO thin films on STO substrates, including, (a) 0 mole %, (b) 1 mole %, (c) 3 mole % and (d) 5 mole % Ir added YBCO samples.



Figure 3. AFM images of (a)undoped and (b) 3 mole% Ir added YBCO thin films on STO substrate.

The dependence of critical transition temperature (T_c) and transition width (ΔT_c) on the amount of BIO in YBCO thin films is given in Figure 4. The T_c value was 87.3 K for an undoped YBCO sample and

it increased with addition of BIO at the same fabrication conditions. They were all close 92 K and the maximum T_c value 92.5 K obtained with the addition of 5 mole % BIO. In addition, ΔT_c values of these YBCO films were firstly increased with 1 mole % BIO addition but then it decreased linearly.



Figure 4. Dependence of critical temperature and transition width on the amount of BIO in YBCO thin film.

4. Conclusion

In this study, production and characterization of undoped and BIO doped YBCO superconductor thin films on STO substrates were investigated by using TFA-MOD technique. Acetate based precursor chemicals were used to produce thin film. In XRD patterns, generally the major peaks correspond to the (001) reflections of the YBCO phases and (100) STO substrate which indicates that the films have a strong c-axis texture. In general speak the surface morphologies of all samples have continuous, flat and crack free surfaces. However some a-axis oriented grains are observed for undoped YBCO film. For BIO doped YBCO films present a denser surface structure compared with the undoped YBCO films. The critical transition temperature of samples was determined by using four wire method. High T_c (>91K) and low ΔT_c values were obtained for all BIO added YBCO thin films.

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