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ARTICLE

Effect of Oxygen Content in Atmospheres of Heat Treatment on the Properties of YBCO Thin films

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Abstract: $YBa_2Cu_3O_{7-x}$ (YBCO) films were prepared on single-crystal $LaAlO_3$ (100) substrate using a low-fluorine sol-gel method. The effect of the oxygen content in the atmospheres of heat treatment at 725 ℃ on the critical current density (J_c) of the obtained YBCO films was investigated. Results show that all the films heat-treated in the oxygen content range of 100~1700 μL/L exhibit good biaxial-texture characteristics. However, high-J_c YBCO films are not obtained at the oxygen contents of 100 and 200 μL/L due to the lower density of the surfaces. With increasing the oxygen content, the film surface becomes dense gradually. When the oxygen content is 300 μL/L, the surface of the film is very dense and J_c reaches 4.3 MA/cm^2. Furthermore, many copper-rich second phases grow up on the surfaces with further increasing oxygen content up to 800 and 1700 μL/L, which is a dominant reason for the decline in J_c of the films.

Key words: superconducting film; sol-gel; low-temperature heat treatment; texture; oxygen content

The fluorine-contained sol-gel method is an attractive candidate for preparing $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting films or coated conductors because the method is of high repeatability in fabricating YBCO films with excellent superconducting properties (T_c > 91 K, J_c > 1 MA/cm^2)[1,2]. Regarding the numerous superconducting thin film architectures for practical applications, such as the multilayer structure in superconducting electronics and the coated conductor on a buffered metal substrate tape, it is desirable to fabricate YBCO films on an insulating or conducting barrier layer[3-5]. Currently, the common heat-treatment temperature for YBCO films derived from the sol-gel method is around 800 ℃ [6,7]. At such high temperature, the interdiffusion between the barrier layer and the YBCO film is probable, which will deteriorate the superconductivity dramatically. Thus, a low-temperature heat treatment is required [8]. The Araki group fabricated superconducting YBCO film at the heat-treatment temperature of 725 ℃ [9]; however, the effect of the growth parameters at 725 ℃ on the characteristics of YBCO film is scarce.

Hammond and Bormann[10] produced an oxygen partial pressure-temperature (P_{O_2}-T) phase diagram according to various in-situ deposition experiments; the diagram revealed that the forming temperature (T) of YBCO film could be decreased by lowering the oxygen partial pressure P_{O_2} in the growing environment. However, the P_{O_2}-T relationship derived from the ex-situ process of electron-beam co-evaporation (BaF_2 process) deviates from the in-situ deposition line[11]. Due to the lack of experimental data, whether the P_{O_2}-T relationship of a sol-derived YBCO film heated at a relatively low temperature follows the in-situ or the ex-situ deposition line remains undetermined. Furthermore, in our previous research an advanced low-fluorine sol-gel method was proposed for preparing high-J_c YBCO film[12], in which the pyrolysis time was shortened drastically due to the reduction of fluorine greatly in the precursor solution. In the present paper, based on the low-fluorine sol-gel method, the oxygen content during heat treatment at 725 ℃ was explored in order to obtain high-J_c YBCO films at a low heat-treatment temperature.

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1 Experiment

The precursor solution of YBCO films was obtained by dissolving fluorine-contained yttrium, non-fluorine barium, and non-fluorine copper acetate salts into methanol with the help of acrylic acid[12]. The total metallic ion concentration of the synthesized precursor solution was 1.2 mol/L. With a single crystal $LaAlO_3$ (100) as a substrate, all of the dip-coated gel films were pyrolysised at 450 ℃ in the same batch. Moisture was introduced by bubbling deionized water with the dew-point temperature of 40 ℃. The whole heat-treatment profile is shown in Fig.1. After the pyrolysis, many nanocrystallines of the metal fluoride and oxide formed. In order to avoid growing up of the nanocrystallines, the pyrolysed film must be cooled down to at least 200 ℃ rapidly. After that, the gas was switched to the mixed gas of nitrogen and oxygen with different O_2/N_2 ratios. The flow rates of nitrogen and oxygen were controlled by a precision mass flowmeter, which enabled an oxygen content of 100~1700 μL/L to be achieved. Then, the samples were heated to 725 ℃ for 100 min in the mixed gas with different oxygen contents. After that, all of the films were oxygenated at 450 ℃ for 2 h in the same batch, which transformed the YBCO into an orthogonal structure with superconducting properties.

The thicknesses of all of the YBCO films were measured by a Surfcorder-SE3500 surface profiler, and the results indicated that all the film thicknesses were approximately 200 nm due to the use of the same solution and withdrawal rate. A SmartLab X-ray diffractometer in θ-2θ, ω, and φ scan modes was used to determine the film phase, the out-of-plane and in-plane texture, respectively. Scanning electron microscopy (SEM) experiments were performed on a Merlin Compact after depositing conductive Pt onto the surface of the films. A VersaLab multi-function vibrating sample magnetometer was used to measure the magnetic moment m under a varying magnetic field, and then, J_c was calculated using the extended Bean model, as given by Eq.(1) [13]:

$$J_c=20\Delta m/[Va(1-a/3b)] \quad (1)$$

Where Δm is the vertical width in the m-B loop in a certain field and V, a and b ($a < b$) are the volume, the width and length of the samples, respectively. The size of the films used in the magnetization measurement was 2.5 mm × 3.0 mm. The temperature was fixed at 77 K, and the applied field with magnetic strength of 0~3 T was perpendicular to the film surface during the measurement.

2 Results and Discussion

2.1 J_c of YBCO film

Fig.2 shows the dependence of critical current density (J_c) of YBCO films on the magnetic field B. It can be seen that the J_c of the film in the entire applied field range of 1~3 T increases at first and then decreases with raising the oxygen content from 100 to 1700 μL/L. When the oxygen content is 300 μL/L, J_c of the YBCO film reaches 4.3 MA/cm^2. The J_c value is larger than that reported by Araki group[9], which could be correlated with the larger oxygen content adopted in this study. The oxygen content of 300 μL/L can be converted to the oxygen partial pressure of about 30 Pa according to the total gas pressure close to 10^5 Pa. The heat-treatment parameter of 725 ℃/30 Pa is just on the thermodynamic equilibrium line corresponding to the tetragonal phase $YBa_2Cu_3O_{6.09}$ (it is not the final composition, which is just one after heat treatment without further oxidation) in $\log P_{O_2}$-1000/T diagram[11,14,15]. Commonly, J_c of YBCO film is relatively high when the heat-treatment parameters on the thermodynamic equilibrium line are adopted. Therefore, the 725 ℃/300 μL/L could be considered as alternative parameters for fabricating high-J_c YBCO film at 725 ℃.

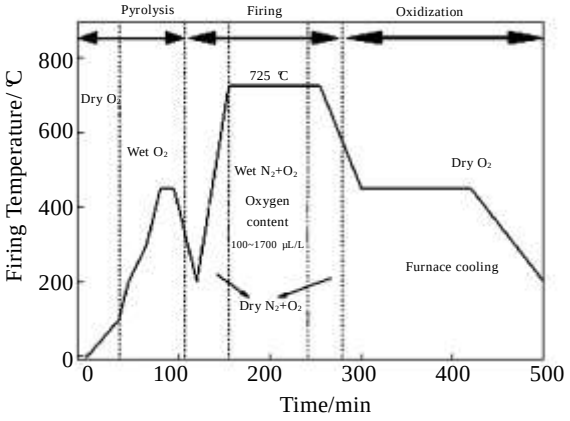

Fig.1 Profile of the heat treatment for preparing YBCO films

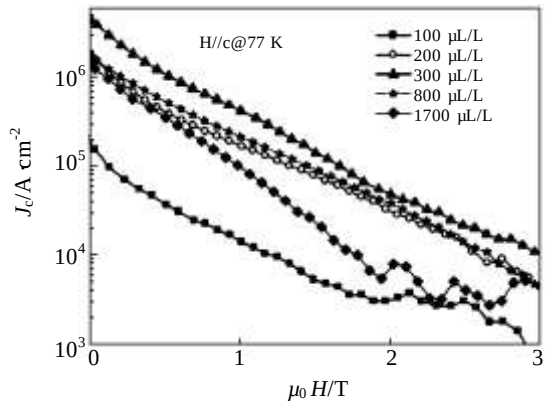

Fig.2 J_c-B relationship of YBCO films heat-treated under different oxygen contents

2.2 Reasons for the change of J_c with the oxygen content during heat treatment

It is well known that the purity and biaxial texture of YBCO film are important factors on the J_c of the film. In order to explore the reasons for the change of J_c with the oxygen content during heat treatment, θ-2θ scans of X-ray diffraction were carried out on the films and the results are shown in Fig.3. It is seen that apart from the diffraction peaks of the substrate and YBCO (00*l*), nearly no peaks due to other phases or non-*c*-axis-oriented YBCO were detected, indicating that the YBCO films exhibit good purity and *c*-axis-preferred orientation.

To evaluate the out-of-plane and in-plane orientation, ω- and Φ scans of X-ray diffraction were conducted on the crystal planes (005) and (103) of the YBCO films, respectively. The dependence of the calculated full width at half maximum (FWHM) values of ω- and Φ scans on the oxygen content is shown in Fig.4. It is found that FWHM values of ω- and Φ scans are relatively large under the oxygen contents of 100 and 200 μL/L, while FWHM values become lower at 300 μL/L and tend to be uniform with further increasing the oxygen content. According to Ref.[10], the driving force for nucleation is weak under tiny oxygen content, leading to relatively less formation of YBCO grains and thereby to relatively weak diffraction peaks and large FWHM values. However, the FWHM values of ω- and Φ scans fall in the scale of 0.5°~0.9° and 1.4°~2.3°, respectively. Such small-scale variation in FWHM values are not enough to change J_c obviously, so the variation of J_c is likely to be relative to other factors such as the surface morphology.

Surface quality is also a significant factor on J_c of YBCO film. Thus, surface morphologies of YBCO films were examined, which is shown in Fig.5. It is seen that many pores appear on the surface of YBCO film when the oxygen content is 100 μL/L, which is responsible for the lower J_c. In this case, the driving force is not enough to form uniform YBCO films due to the too-low oxygen content[10]. With increasing the oxygen content, the film surface becomes denser. When the oxygen content is 300 μL/L, the surface is very dense, resulting in the enhancement of J_c. However, with further increasing the oxygen content up to 800 and 1700 μL/L, several large particles form on the film surface. By the energy dispersive spectroscopy (EDS) analysis, the large particles are proved to be copper-rich phases. According to the Ref.[10], high oxygen content allows for cluster formation of metal oxides on the surface due to the enhancement of the driving force for nucleation. Therefore, many copper-rich particles appear on the film surface. These copper-rich phases are likely to induce the deviation of film composition at localized areas, thereby leading to decline of J_c.

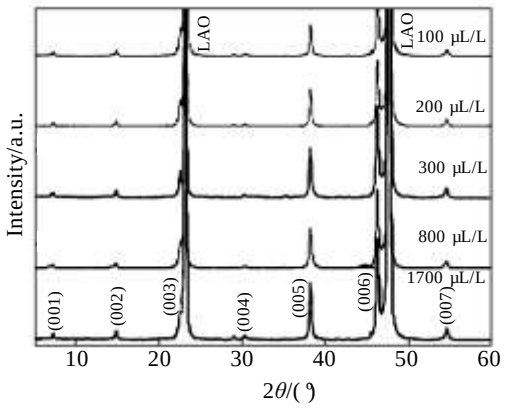

Fig.3 θ-2θ scan of XRD for YBCO films heat-treated under different oxygen contents

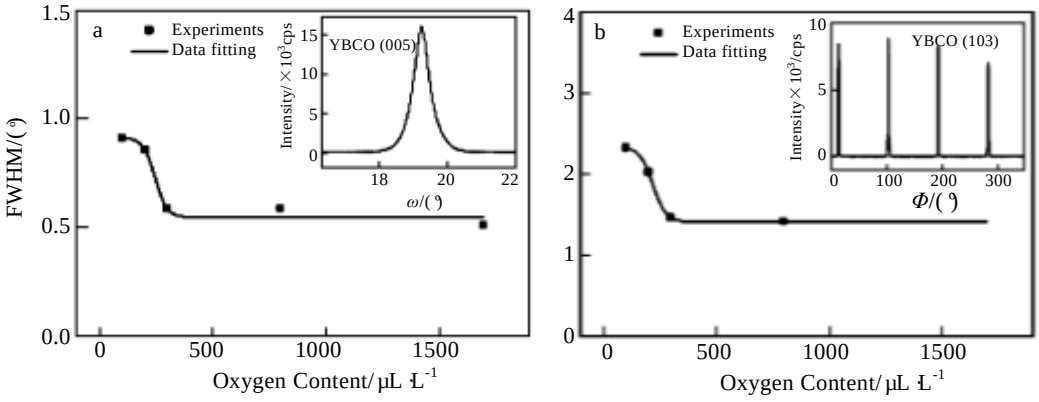

Fig.4 FWHM dependence of ω- (a) and Φ (b) scans on the oxygen content during heat treatment for YBCO films. (the insets are original results of ω- and Φ scans for the sample heat-treated at the oxygen content of 300 μL/L)

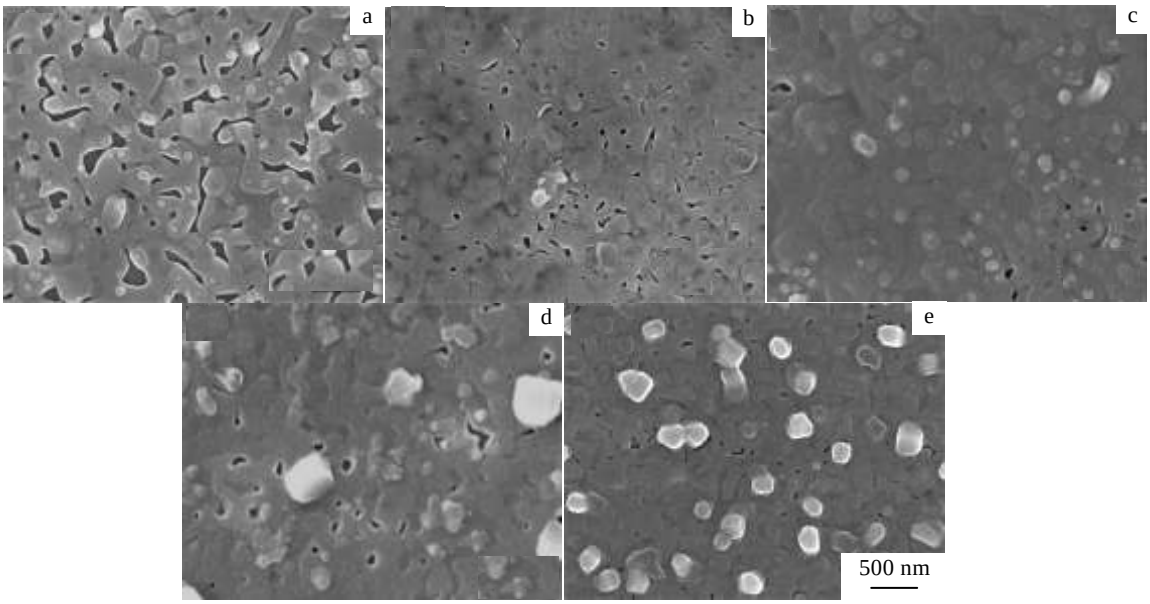

Fig.5 Surface morphologies of YBCO films heat-treated at the oxygen contents of 100 μL/L (a), 200 μL/L (b), 300 μL/L (c), 800 μL/L (d), and 1700 μL/L (e)

3 Conclusions

1) The surface of YBCO film becomes denser with increasing the oxygen content in the range of 100~1700 μL/L, but copper-rich second phases grow up gradually.

2) When the oxygen content is 300 μL/L, the YBCO film exhibits good density, only a few second-phase particles appear on the surface, and J_c reaches 4.3 MA/cm^2.

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热处理气氛中氧含量对 YBCO 薄膜性能的影响

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摘　要：采用低氟溶胶-凝胶法在$LaAlO_3$(100)基板上制备了$YBa_2Cu_3O_{7-x}$ (YBCO)薄膜，研究了在725 ℃热处理过程中，氧含量对最终所得YBCO薄膜临界电流密度J_c的影响。研究发现，热处理过程中氧气含量在100~1700 μL/L范围变化时，所获得的YBCO薄膜均具有良好的双轴织构特征。然而，当氧气含量为100或200 μL/L时，由于YBCO薄膜致密性差，不能获得高J_c的YBCO薄膜。随着氧气含量的增大，YBCO薄膜表面逐渐变得致密。当氧气含量增加到300 μL/L时，YBCO薄膜表面较致密，J_c达到4.3 MA/cm^2。继续增大氧含量至800和1700 μL/L，薄膜表面逐渐出现富铜第二相颗粒，成为其J_c较低的主要原因。

关键词：超导薄膜; 溶胶-凝胶; 低温热处理; 织构; 氧含量

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