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Oxygen diffusion in *c*-textured epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films^①

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[Abstract] Isothermal oxygen diffusion in *c*-textured epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films was studied by in situ X-ray diffraction. Thermal expansion coefficients of *c*-axis length with different oxygen contents are $\alpha_c(6.91, \text{O}_2) = 19.1 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_c(6.0, \text{N}_2) = 19.3 \times 10^{-6} \text{ K}^{-1}$ respectively. Chemical diffusion process of oxygen was described by relaxation time. From the Arrhenius plot of relaxation time, an activation energy of lattice diffusion was obtained as 1.1 eV, which is close to the results of SIMS (0.95 eV) and internal friction (1.02 eV).

[Key words] oxygen diffusion; in situ X-ray diffraction; relaxation time

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1 INTRODUCTION

Ever since the introduction of physical vapor deposition to the epitaxial growth of high temperature superconducting cuprates, the quality of the material has been greatly improved^[1,2]. At present, high quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films with $T_C > 90 \text{ K}$, $J_C > 10^6 \text{ A/cm}^2$ at 77 K can be easily prepared by either laser ablation or by magnetron sputtering on (100) SrTiO_3 or (100) LaAlO_3 substrates^[1]. In these two processes, stoichiometry of the material is warranted by the application of a single $\text{YBa}_2\text{Cu}_3\text{O}_7$ target and full oxidation is secured by a post annealing in oxygen atmosphere^[3]. The oxidation process is also essential to raise T_C to above 90 K, because the structure and superconducting state of the unique oxide strongly depend upon the oxygen stoichiometry, i. e., oxygen deficiency δ ^[4]. The oxidation process is decided by the behavior of oxygen diffusion. Therefore, detailed studies of oxygen diffusion in YBCO films are not only necessary because the magnitude of the oxygen diffusion coefficient is one of the most critical parameters in optimization of the preparation process, but also quite valuable in elucidating the unusual defect structure of this oxide^[5].

Electrical resistance measurement^[6~8], thermogravimetric analysis (TGA)^[9], low-frequency internal friction^[5], second ion mass spectroscopy (SIMS) profiles of O^{18} tracer^[10,11] have been applied to investigate oxygen diffusion in powder, polycrystalline and single crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The widely accepted facts about oxygen diffusion are: 1) the anisotropic nature of oxygen diffusivity, $D_{ab} \approx (10^5 \sim 10^6) D_c$; 2) the structure transformation occurs at $\delta = 0.6 \sim 0.7$, the phase transition is controlled by oxygen dif-

fusion kinetics; 3) oxygen is long-range ordered in the orthorhombic phase and short-range ordered in tetragonal phase^[4,11]. But there is still wide divergence of values reported^[10]. More recent reports on diffusion constants tended to hover near 10^{-11} to $10^{-13} \text{ cm}^2/\text{s}$ at 500 °C^[9]. The activation energy ranges from 0.3 to 1.7 eV^[6~9,11]. Different microstructures of polycrystalline specimens, especially porous and cracks of the specimens, lead to the discrepancy.

Relatively less results of oxygen diffusion in YBCO films is available because of the difficulty of direct quantitative measurement of oxygen content in films^[7,8,11~13]. In situ electrical resistance measurement is a convenient method for measuring oxygen diffusion in thin film through the relationship between conductivity and oxygen content, but the relations were obtained on equilibrium samples, so it is not effective or not precise enough for samples during oxygen chemical diffusion, especially for the large variation of oxygen content during oxygen diffusion process^[8]. In the present work, real-time oxygen content in *c*-axis oriented YBCO films were measured by in situ X-ray diffraction according to the well established curve^[4] between oxygen content $7-\delta$ and *c*, *c*-axis length, during oxygen diffusion, thus eliminating such influence of electrical resistance measurement.

2 EXPERIMENTAL

Highly crystalline *c*-textured epitaxial sputtered YBCO thin films of 3 mm × 10 mm size and 300 nm thickness on (100) SrTiO_3 substrate were used. Good *c*-axis orientation of the films was verified by Bragg-Brentano diffraction pattern and (005) rocking

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curves. The preparation and properties of the films were described elsewhere^[3].

Rigaku D/Max-RB X-ray diffractometer equipped with a high temperature chamber was applied to in situ monitoring the move of (0010) diffraction peak during oxygen diffusion procedure. The specimen used for oxidation was loaded into the chamber of the diffractometer and was firstly deoxidized in nitrogen at 450 °C to reduce oxygen content to an unchangeable stoichiometry of 6.0, that is $\delta = 1$. Then the temperature was lower to the oxidation temperature and 2θ of (0010) peaks were continuously taken in situ as oxidation time proceeds.

Measurement of thermal expansion coefficient of *c*-axis length *c* in the thin films was carried out through YBa₂Cu₃O_{6.91} within oxygen atmosphere, YBa₂Cu₃O_{6.0} within nitrogen atmosphere from 250 to 400 °C holding for 10 min at an interval 25 °C.

3 RESULTS AND DISCUSSION

The relationships between *c*-axis length *c* and temperature relative to room temperature are shown in Fig. 1. Thermal expansion coefficients of *c* for YBa₂Cu₃O_{6.91} within oxygen and for YBa₂Cu₃O_{6.0} within nitrogen are $\alpha_c(6.91, O_2) = 19.1 \times 10^{-6} K^{-1}$ and $\alpha_c(6.0, N_2) = 19.3 \times 10^{-6} K^{-1}$, respectively, through simple linear regression. The value is similar to $23 \times 10^{-6} K^{-1}$ ^[13] and $19 \times 10^{-6} K^{-1}$ ^[4]. The different thermal expansion coefficients of *c*-axis length *c* in different oxygen content specimens would be the result of different *c* values of orthorhombic and tetragonal phases. α_c does depend on the oxygen content, i. e., oxygen deficiency δ . For simple treatment of data, $\alpha_c(6.0, N_2) = 19.3 \times 10^{-6} K^{-1}$ was used to calibrate *c*-axis length *c* of film against room temperature. By the relationship between oxygen content $7 - \delta$ and *c*, *c*-axis length, oxidation curves for 3 samples at different temperatures are shown in Fig. 2. Data for 300 °C (in solid diamonds) from the

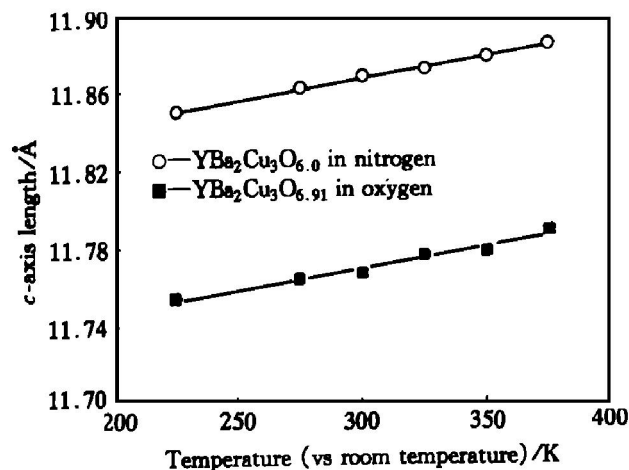


Fig. 1 Relationship between *c*-axis length *c* and temperature relative to room temperature

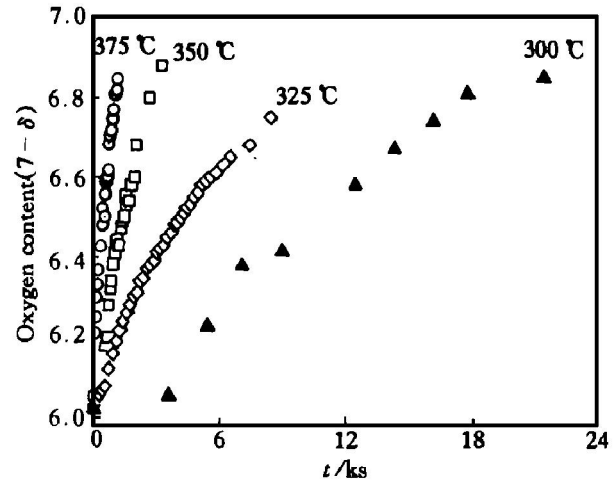


Fig. 2 Relationship between oxygen content $7 - \delta$ and oxidation time

Ref. [12], which were gained by quenching sample oxygenated at 300 °C for certain time and measuring at room temperature, are also shown in Fig. 2.

It is well known that variation of the external conditions (temperature or oxygen pressure) leads to the process of oxygen diffusion for YBCO. As the external conditions vary, the relaxation time τ , which is the characteristic time from one equilibrium state to another, can be related to the diffusivity through the diffusion length: $L^2/D \propto \tau$ ^[8].

According to the diffusion theory, when the diffusion time is long enough, no matter in which geometric shape oxygen diffuse, the relationship between normalized oxygen content α and oxidation time *t* can be written in the unified form:

$$\alpha = \frac{\delta(t) - \delta(\infty)}{\delta(0) - \delta(\infty)} \approx A \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where $\delta(0)$ and $\delta(\infty)$ are the initial and final equilibrium oxygen contents; $\delta(t)$ is the oxygen content at *t* during oxidation; *A* is the geometric shape factor, which is related to the microstructure of the films. In order to obtain the value of τ , Eqn. (1) is rewritten as follows:

$$\ln \alpha = \ln \frac{\delta(t) - \delta(\infty)}{\delta(0) - \delta(\infty)} = \ln A - \frac{t}{\tau} \quad (2)$$

All the oxidation curves are normalized according to Eqn. (2). Fig. 3 shows the linear relationships between $\ln \alpha$ and *t* for four different temperatures. The reasons for the four straight lines not intersecting one point at longitudinal axis are a little difference of microstructure between specimens used for four temperatures and the data of 300 °C measured at room temperature lead to much more experimental error. From the slope of each straight line in Fig. 3, the relaxation time τ of each temperature is gained. The Arrhenius plot of τ is shown in Fig. 4. The activation energy *E* for lattice diffusion obtained from Fig. 4 is 1.10 eV, which is close to that measured by internal friction (1.02 eV)^[5] and SIMS (0.95 eV)^[10].

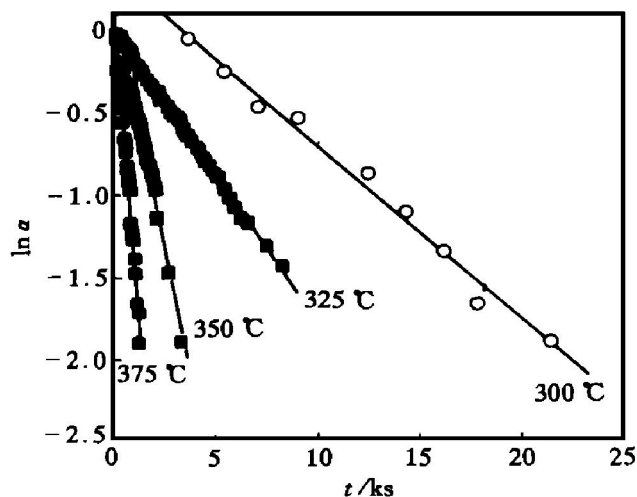


Fig. 3 Normalized oxygen content vs oxidation time

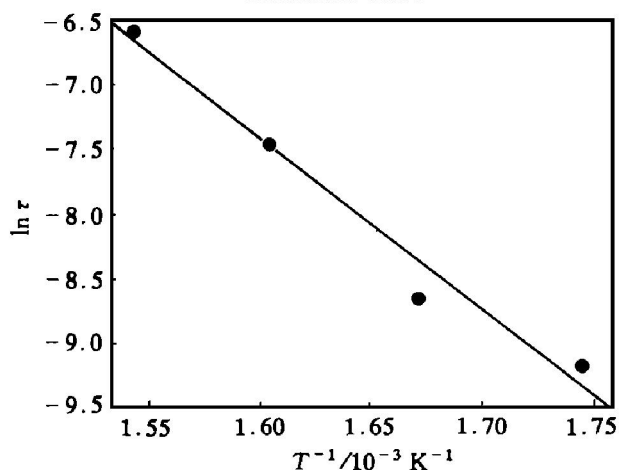


Fig. 4 Arrhenius plot of τ

It is widely accepted that oxygen diffusion in YBCO is planar and is limited to Cu(1)-O basal planes by atomic jumps between sites O(1) and O(5). Oxygen diffusion is highly anisotropic, diffusivity in the basal plane is much larger than that parallel to c -axis, i. e. $D_{ab} = D_c \gg D_{\parallel c}$ ^[10]. Diffusion along c -axis involves oxygen exchange between sites O(4) and O(2) or O(4) and O(3), which is not permitted. So it is concluded that the free surface of the c -texture YBCO films is intrinsically impervious to oxygen diffusion.

If the films are considered ideal perfect crystal, oxygen diffusion can be counted by lattice diffusion in ab basal plane alone from four edge sides of the films to interior. The full oxidation time at 350 °C is estimated by the simple relationship: $t = X^2/4D$. In experimental condition, $X = 3/2 \text{ mm} = 1.5 \text{ mm}$, $D = 2 \times 10^{-11} \text{ cm}^2/\text{s}$ (350 °C), so $t \approx 12000 \text{ d}$, which is much longer than that necessary for actual oxidation at the same temperature. The fact suggests that there are fast diffusion pipes in thin films. According to the result of (005) rocking curve^[3], it is indicated that the films consist of mosaics with a 0.3° spread of c -axis. Small angle tilting boundary, which consists of a rather uniform stacking of edge dislocations into a

wall with the dislocation lines perpendicular to c -axis, form at interface between two mosaics. Edge dislocations in the subgrain boundaries with their ends emitting on the four side planes serve as the fast diffusion pipes. The relationship between dislocation structure of thin films and oxygen diffusion will be further studied.

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