Preferential Growth and Peculiar Interfacial Atomic Configuration of the YBCO Liquid-Phase Epitaxial Film with 45° In-Plane Alignment

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ABSTRACT: Using 8-fold symmetric YBa2Cu3O7−x (YBCO, Y123) superconducting films, researchers always encounter the problem of multiple in-plane orientations of the deposited c-axis epitaxial YBCO grains with respect to the substrate, particularly in films prepared by vapor deposition on MgO. Usually, two prevailing in-plane alignments, denoted as 0° ((100)YBCO|(100)MgO) and 45° ((110)YBCO|(100)MgO), have been observed and deduced to be the most favorable ones in terms of the geometrical lattice matching.1,2 So far, the liquid-phase epitaxy (LPE) experiments also indicated that the 0° YBCO grains possess more stability than the 45° grains because the resulting films only present the sole 0° in-plane alignment by using a 8-fold symmetric seed film (containing both 0° and 45° grains).3 Many numerical calculations taking into account aspects of geometrical coincidence and Coulomb force factors were in good agreement with the LPE results.4 Nevertheless, most of these LPE experiments were performed in air atmosphere and the atmosphere factors have not been considered. Here we note that the pure oxygen environment has proved to exhibit dominant influence on the thermal stability of the in-plane alignment of YBCO films under different oxygenation conditions. Field-dependent critical current density of pure 45° and 0° YBCO films was measured and compared. Thus, the effect of the interfacial structure on critical current density was inferred.

1. Introduction

In growing YBa2Cu3O7−x (YBCO, Y123) superconducting films, researchers always encounter the problem of multiple in-plane orientations of the deposited c-axis epitaxial YBCO grains with respect to the substrate, particularly in films prepared by vapor deposition on MgO. Usually, two prevailing in-plane alignments, denoted as 0° ((100)YBCO|(100)MgO) and 45° ((110)YBCO|(100)MgO), have been observed and deduced to be the most favorable ones in terms of the geometrical lattice matching.1,2 So far, the liquid-phase epitaxy (LPE) experiments also indicated that the 0° YBCO grains possess more stability than the 45° grains because the resulting films only present the sole 0° in-plane alignment by using a 8-fold symmetric seed film (containing both 0° and 45° grains).3 Many numerical calculations taking into account aspects of geometrical coincidence and Coulomb force factors were in good agreement with the LPE results.4 Nevertheless, most of these LPE experiments were performed in air atmosphere and the atmosphere factors have not been considered. Here we note that the pure oxygen environment has proved to exhibit dominant influence on the out-of-plane orientation of the YBCO films,5 which made us believe that varying oxygen environment may play some role in the stability of YBCO grains with various in-plane alignments.

Moreover, preparation of YBCO films with a pure 45° in-plane orientation is more difficult than that of the 0° ones, and thus information concerning the 45° YBCO/MgO interface is very limited in literature. As the structure and energies at the film−substrate interface are considered to affect the film growth, it is important to unveil the 45° YBCO/MgO interface configuration and make comparison with the 0° case. Matsuda et al.5* found that the YBCO films with 0° in-plane orientation and NdBCOx films with 45° in-plane orientation are terminated by BaO and CuO-chain layers at the interfaces, respectively. The NdBCOx grains with the 45° in-plane orientation exhibited a better thermal stability during growth in air. Buchholz et al.5† proposed a method for how to control the in-plane orientation of the YBCO thin film grown in the vapor deposition system on MgO substrate by means of a properly chosen thickness of a predeposited BaO layer. The 45° YBCO thin films were obtained by the predeposition of a relatively thin BaO layer (<7 × 1015 Ba/cm2), where the interface is dissimilar with the “true” 45° YBCO/MgO interface.

In the present paper, we report on our attempt to grow YBCO films by LPE in a pure oxygen environment using an 8-fold symmetric YBCO seed film. In order to decipher the underlying mechanism, high-resolution transmission electron microscopy (HRTEM) was employed to identify the interface structure between the 45° LPE film and substrate. In addition, comparison of the field dependence of Jc in the pure 45° and 0° YBCO LPE films was made. The possible correlation between the in-plane alignment and superconducting properties of the YBCO films is discussed.

2. Experimental Section

The 8-fold symmetric YBCO thin films were fabricated by vapor deposition on MgO (100) substrates. The LPE growth was performed in pure oxygen atmosphere with the Ba:Cu = 3:5 melt. The in-plane texture of both the seed films and the LPE ones was evaluated by X-ray diffraction measurements and polarized Raman spectroscopy. The transverse cut specimen for transmission microscopy was prepared by mechanical polishing, followed by ion milling on a liquid-nitrogen-cooled stage. Electron diffractions and HRTEM images were obtained with the JEOL-2010 electron microscope with the point-to-point resolution of 0.194 nm. The critical transition temperature (Tc) and magnetization hysteresis curves in magnetic fields up to 8 T (H//c-axis) were measured with the vibrating sample magnetometer (VSM) insert of a PPMS-9 system (QD). The Jc values were evaluated using the extended Bean model from the irreversible magnetization.7

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3. Results and Discussion

The in-plane alignment of YBCO seed film was tested by the X-ray \( \phi \)-scan and polarized Raman spectroscopy. The \( \phi \)-scan is shown in Figure 1. The seed film turned out to possess the typical 8-fold symmetry. Figure 2 shows the optical image of the YBCO thick film grown epitaxially on the 8-fold symmetry seed film in 1 atm pure oxygen atmosphere. Evidently, only the square growth spirals with the uniform 45° azimuth with respect to the [100] MgO orientation can be observed by optical microscopy. It is surprising that the in-plane orientation of the LPE film looks opposite to the preferential growth orientation in air, at least at the first glance. In order to confirm this result, the polarized Raman spectroscopy was utilized for characterization of the LPE film.

Many articles, for example, refs 8–10, reported on the sensitivity of the Raman peak around 340 cm\(^{-1}\) (O2-+O3- \( \leftrightarrow \) B\(_{1g} \) mode) to rotation of the polarization \((\vec{e}_i, \vec{e}_s)\) in increments of 45°. We decided to use this effect to determine the in-plane orientation of the YBCO material. In Figure 3a one can see that the peak around 340 cm\(^{-1}\) almost vanishes, when the polarization \((\vec{e}_i, \vec{e}_s)\) lies along the [100] or [010] axes of the MgO substrate, while for \((\vec{e}_i, \vec{e}_s)\) parallel to the MgO [110] or [1\( \bar{1} \)0] directions the peak magnitude remains relatively high. Further, the pole-image profile of the LPE film in Figure 3b clearly confirms that the YBCO LPE film is purely in-plane 45° oriented.

We also studied the influence of the growth atmosphere on stability of 0° and 45° grains. The atomic configuration at the 45° YBCO/MgO interface was therefore investigated by HRTEM. Two kinds of atomic configurations near the interface were found. Figure 4a shows a typical cross-sectional HRTEM image of the 45° YBCO film. As mentioned above, in the 0° YBCO/MgO interface the terminal layer was identified as the BaO layer.\(^2\) In the present case, the interface is terminated by the CuO chain (see Figure 4b). The CuO chain layer introduces an intensive distortion to the lattice and mismatch between YBCO and the MgO crystal. As reported in ref 2 in 45° NdBCO grains, the bottom layer at the MgO substrate was also found to be the CuO chain layer. From the point of view of energetic stability, it is reasonable to compare the structural features of NdBCO and YBCO grains. First, formation of the bottom layer can be considered as an atomic cut between two layers. For instance, the BaO bottom layer can be regarded as a cut between BaO and CuO\(_2\) layers, while the CuO chain bottom layer can be considered as a cut between CuO and BaO layers. The bottom layer corresponding to the lowest energy cut is likely to be the most stable one. Second, the position of the lowest energy cut depends on the oxygen status of the particular REBCO lattice. As Granuzzo et al. suggested,\(^1\) in YBCO in the oxygen-deficient state the minimum energy cut along the (001) lies between BaO and CuO\(_2\) layers. On the other hand, in the oxygen-saturated state...
state the lowest energy cut lies between CuO chain and BaO layer. According to the analysis of bottom atomic layer, the 45° YBCO and NdBCO grains are in an oxygen-saturated state due to the CuO chain bottom layer, while the 0° YBCO grains are in an oxygen-deficient one due to the BaO bottom layer. This deduction is in good agreement with the solid-solution properties of NdBCO compound in which oxygen content is regarded higher than in Y123 due to a considerable RE3+/Ba2+ substitution.12 In the YBCO system, it is also reasonable that growth of oxygen-saturated 45° grains is preferred in a pure oxygen environment, which then probably enhances the chemical potential of oxygen in the melt. In other words, in the pure oxygen atmosphere, the interface of the 45° YBCO seed grains with CuO chain terminal layer becomes more thermally stable than the interface of the 0° grains.

Figure 5a presents a HRTEM image of another kind of interface feature observed in the 45° YBCO film. In addition to the well-defined lattice of YBCO, a peculiar layer above the sharp interface was recognized. The blow-up of this area shown in Figure 5b identifies two unexpected rows of atoms between MgO and the BaO-CuO-BaO blocks of Y123. We deduce that these arrays are comprised of Cu2O because (1) Based on the middle-energy ion scattering (MEIS) study, Afrosimov et al.13 pointed out that the occurrence of additional protoxide composition - Cu2O is possible at the YBCO/MgO interface. (2) Although the inserted atomic rows match the MgO substrate well, the atoms are not located right above the Mg atoms but are shifted by about 0.21 nm along ⟨100⟩ MgO. This is in good agreement with the crystal structure of Cu2O14 and, in particular, with the Cu2O (001) thin-film growth on MgO substrate.15 Periodic interstitial Cu atoms within the adjacent BaO layer were also observed with the density of 1 nm⁻¹ along ⟨100⟩ MgO (see Figure 5b), evidently compensating the lattice mismatch. The existence of the Cu2O intermediate layer is to our knowledge a new kind of interfacial structure in 45° grains that might be advantageous for the stability of the 45° YBCO seed grains during LPE in pure oxygen. The Cu2O inserted layer belongs neither to the Y123 lattice nor to the MgO substrate. Therefore, its decomposition temperature may directly influence the thermal stability of seed grains. From the chemical phase diagram, it follows that the melting point of Cu2O increases with the rise of oxygen partial pressure.16 The following simple assumption can be drawn: in air the decomposition temperature of the incomplete Cu2O lattice is lower than of Y123 and thus it negatively affects the stability of the 45° YBCO seed grains. In oxygen, the melting point of the Cu2O layer is remarkably higher than of Y123, which makes the 45° YBCO seed grains more stable than the 0° ones. The different interfacial configuration in 0° and 45° oriented YBCO films is thus considered to be responsible for their different stability. Besides, the different interfacial configuration can also affect in different ways the pinning structure and lead to various electromagnetic properties. For instance, in YBCO films with a predeposited BaO PLD layer,6 critical current density at 78 K was 1.1 × 10⁶ A/cm² in 0° YBCO thin film and 1.7 × 10⁶ A/cm² in a 45° one. Field dependence of critical current density of the LPE YBCO films with pure 0° and 45° in-plane orientation was deduced from the inductively measured M-H curves. While the onset Tc of both 45° and 0° samples was about 90.5 K, the value

Figure 4. (a) A HRTEM image taken near the interface between 45° YBCO film and MgO substrate. (b) The blow-up shows the detailed interface structure, in particular the CuO chain bottom layer.

Figure 5. (a) HRTEM image taken near the interface between 45° YBCO film and MgO substrate. (b) The blow-up indicates the detailed structure including an inserted Cu2O layer and an interstitial Cu atom.

Figure 6. Field dependence of Jc at 77 K of YBCO LPE films with pure 45° and 0° in-plane orientation.
comparable to the reference YBCO films, the \( J_c(H) \) data at 77 K significantly differed. As shown in Figure 6, the remnant \( J_c \) \((\text{H})\) of the 45° film was approximately \(2.5 \times 10^{9}\) A/m², nearly 2 times higher than in the 0° film, \(1.45 \times 10^{9}\) A/m². It resembles a similar \( J_c0 \) data difference in the 0° and 45° YBCO PLD thin films. The underlying mechanism is not yet clear, and more investigation is required to confirm the direct relationship between the critical current density and interfacial configuration. Hopefully, it could be helpful for the optimization of pinning performance of LPE films and coated conductors.

4. Conclusion

In conclusion, the YBCO film with pure 45° in-plane alignment was grown on an 8-fold symmetry seed film by a modified LPE method, under 1 atm oxygen atmosphere. The interfacial atomic configuration was found to be crucial for the 45° preferential growth. Two kinds of interfacial bottom layers on MgO substrate were revealed by HRTEM, one of CuO chain layer and the other of a Cu2O layer inserted between Y123 and MgO. Both interfacial configurations are in agreement with the stability of the 45° YBCO grains exhibited under a pure oxygen environment, with respect to the 0° grains. The remnant \( J_c \) value of pure 45° YBCO films was found remarkably higher than that of pure 0° film, which might have some relationship to the pinning structures facilitated by different interfacial structures.

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