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Microstructure of YBCO thin film and its effect on superheating

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ABSTRACT Previously, we have reported a superheating phenomenon of a YBa2Cu3Ox (YBCO) film and studied its mechanism. In this work, we investigated the influence of microstructure on the superheating of a YBCO thin film. Different melting behaviors were observed in situ from YBCO thin films with varied microstructures by using high-temperature optical microscopy (HTOM). These films with different degrees of crystallinity were also characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD). It was found that the crystalline structure features of the seed film have a great influence on the degree of superheating and the melting behavior. A high-quality film with a low fraction of interface defects is believed to be responsible for the high superheating. On the basis of the experimental results from HTOM, AFM, and XRD, the melting and superheating behaviors associated with the film defect structure are well interpreted in terms of the semi-coherent interface-energy theory.

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1 Introduction

Recently, the superheating phenomenon has been of an increasing scientific and practical concern. According to the theories of superheating, if heterogeneous nucleation at free interfaces or grain boundaries is suppressed, crystals could be superheated above their equilibrium melting points [1–4]. In 1986, Daeges et al. first reported the superheating phenomenon in a system of Ag particles coated by Au, in which the Ag particles could be superheated to 25 K above T0 for 1 min without melting [4]. Since then, the superheating phenomenon has been reported in various systems such as embedded and low-dimensional materials, which are limited to the metals or their alloys [5–8]. In our previous work, we firstly reported a superheating to 50 K above Tp for 3 min occurring in YBa2Cu3Ox (YBCO or Y123) oxide thin films [9, 10], which were deposited on MgO substrates. The origins of this superheating were clarified as below: (1) a low-energy interface of YBCO/MgO due to semi-coherent bonding suppresses the heterogeneous melting nucleation at the interface, which directly induces the superheating. (2) As we know, YBCO oxide material (Y123) decomposes, via the peritectic reaction, into two phases of a Y2BaCuO5 (Y211) solid phase and a Ba–Cu–O (BCO) liquid phase when melting:

Y123(solid) → Y211(solid) + BCO(liquid). This peritectic reaction is reasonably expected to require superheating because of the positive surface energy change due to the formation of the Y211 solid phase. (3) The non-wetting of Ba–Cu–O liquid with both YBCO and MgO causes a liquid migration from the melting front. This behavior leads to suppression of the melting growth, i.e. superheating, because the further melting requires extra driving force after Ba–Cu–O liquid has migrated away.

The concept of superheating as set out above has rationally explained YBCO-seeded NdBCO growth (YSNG) [11, 12], in which the low peritectic temperature of a YBa2Cu3O7 seed film was used for the growth of the high peritectic temperature Nd1+yBa2−x−1Cu4O−1 thick film. This so-called hetero-seeded growth is very promising since it can be extended to a wider application field of YBCO-seeded RE1+yBa2−x−1Cu4O−1 (RE-BCO, RE = rare-earth element) growth, suitable for all RE-BCO systems. In those applications, it is believed that the crystallinity of a YBCO thin film plays a crucial role in affecting the degree of superheating, which further influences the liquid phase epitaxy (LPE) growth mode and the quality of the LPE films. However, there have been few studies of superheating behaviors based on defect structures of YBCO thin films in previous work.

The aim of this work is to investigate the correlation of microstructure with the superheating of YBCO thin films, which may provide more insight into the superheating mechanism. The real-time observations were carried out on the melting of YBCO thin films, which have different structures and crystallinities. High-temperature optical microscopy (HTOM), atomic force microscopy (AFM), and X-ray diffraction (XRD) were used to characterize the film structures. The melting mode and superheating mechanism, associated with the defect structure of the YBCO films, are discussed on the basis of the semi-coherent interface-energy theory.

2 Experimental

The Y123 thin films were deposited on MgO single-crystalline substrates by using the pulsed laser deposition (PLD) technique. The processing parameters were varied
in order to develop different defect structures in the films. The films were labeled as A and B according to their degree of crystallinity. Both films are c-axis oriented and present a relationship between the film and the substrate denoted by
\[
\langle 100 \rangle_{\text{YBCO}} \parallel \langle 100 \rangle_{\text{MgO}}.
\]

Before the melting process, atomic force microscopy was used to observe the surface microstructure. Furthermore, the full width at half-maximum (FWHM) for YBCO (005) peaks was obtained by X-ray diffraction using Cr radiation.

The experimental apparatus for observing the melting behavior consisted of a high-temperature optical microscope (BX51M) and a heating stage (TS1500). The temperature range was from room temperature to 1500 °C, which was calibrated using pure silver shavings (melting at 961 °C). The temperature of the sample was controlled within ±1 °C of the set value by a microcomputer and measured by a Pt/Rh thermocouple. First of all, the specimen was fixed onto a sapphire, which was set on the bottom of the heating furnace. Subsequently, the heating procedure started at room temperature and terminated at 1070 °C. As shown in Table 1, the whole heating process consists of several stages with different heating rates. Due to poor thermal conduction of the specimens, a low heating rate was preset after reaching 960 °C and the temperature was held at several fixed points to ensure that the displayed temperature was coincident with the real temperature of the film. All experiments were carried out in air atmosphere. Furthermore, after the specimen was cooled to room temperature at a high rate and taken out of the heating stage, the surface morphology was observed by optical microscopy to make a clearer comparison between film A and film B.

3 Results and discussion

In Fig. 1, two groups of micrographs are taken at several characteristic points, which explicitly illustrate the comparison of the melting process between YBCO thin films A and B. As we can see, these two groups of optical micrographs mostly show dissimilar features when the samples are at the same temperature. Figure 1 A (1) shows the microstructure of film A after holding for 3 min at 1010 °C; the melting apparently does not occur at this stage. The black dots on the film A can be considered as the impurities in YBCO crystal. The micrograph shown in Fig. 1 B (1) is approximately the same as Fig. 1 A (1).

During the period of heating from 1010 °C to 1050 °C, there is no obvious change in both samples. From Fig. 1 A (2), we can observe that a few acicular \(Y_2BaCuO_5\) (Y211) crystals gradually appeared from the undersurface after the film A was held for 3 min at 1050 °C, which is higher than the peritectic temperature of YBCO \((\sim 1010 °C)\). But, the majority of the YBCO thin film keeps the same morphology as at the beginning, implying that an extensive melting behavior has not taken place yet. Subsequently, Fig. 1 A (3) gives an optical micrograph of film A when the temperature reaches 1060 °C, which is similar to the former one. It indicates the superheating of YBCO oxide.

In comparison, film B exhibits a different evolution in its melting. The micrographs shown in Fig. 1 B (2) and Fig. 1 B (3) can be generally described as follows: the melting of Y123 crystal is proceeding with a higher rate during the period from 1050 °C to 1060 °C. As can be seen in Fig. 1 B (3), when the temperature of the YBCO thin film B reaches 1060 °C, the melting has been proceeding simultaneously. The peritectic reaction occurs over most of the area of the surface, implying that the melting of film B nucleated simultaneously everywhere. In short, during this heating stage, there exists a distinct difference between two samples A and B, not only in the morphology of the surface, but also in the nucleation behavior.

After holding for 3 min at 1060 °C, we can observe that well-aligned Y211 grains continue to nucleate and grow on a MgO substrate from Fig. 1 A (4). As the result of the YBCO decomposition, molten BaCuO covers the Y211 grains due to its high wettability to Y211 and low wettability to the MgO substrate. It should be noted that the un decomposed YBCO particles are still clearly visible, especially in the large space between two Y211 grains. In contrast, all Y123 grains in film B have decomposed into the Y211 solid phase and the BaCuO liquid phase; the image of film B is absent because the peritectic reaction has been accomplished. It is remarkable that the degree of the superheating of film A is much higher than film B. In fact, in our further observation, it is found that the YBCO grains of film A have completely decomposed when the temperature reaches 1070 °C.

In brief, there are two points that must be emphasized from the in situ observation of the melting process mentioned above: (1) film A can be superheated to a higher temperature than that of film B. (2) The behavior of melting nucleation on each film is quite different. On the basis of these two characteristics, we have performed a careful investigation by combining the microstructure analysis with the semi-coherent interface-energy theory as follows.

Generally, it is often very difficult to achieve a perfect in-plane alignment for YBCO seed films prepared by vapor deposition methods and they usually consist of differently oriented in-plane and polycrystalline crystals. In order to study the relationship between the microstructure of YBCO seeds and the degree of superheating, we analyzed films A and B by means of the AFM method. As shown in Fig. 2a, the YBCO grains in film A have a relatively regular square shape. Those specific grains indicated by arrows are the so-called a-axis-oriented YBCO grains, which are reported by Nomura et al. [13]. Similar to strain relaxation of gadolinium-doped ceria \((Ce_{0.8}Gd_{0.2}O_{2-δ})\) thin films by precipitated nanoparticles which have a Ga-rich composition of \(Ce_{0.7}Ga_{0.3}O_{2-δ}\), reported by Huang et al. [14], in our case, taking lattice match-

<table>
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<th>Heating speed (°C/min)</th>
<th>Limit (°C)</th>
<th>Holding time (min)</th>
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<tbody>
<tr>
<td>80</td>
<td>960</td>
<td>3</td>
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<tr>
<td>5</td>
<td>1010</td>
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<td>5</td>
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TABLE 1 The heating procedure of the YBCO seed film