Real-time observation of the melting process of YBCO thin film on MgO substrate

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Abstract
In order to study the mechanism of the liquid phase hetero-epitaxial growth, the melting process of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films was observed by high-temperature optical microscopy. During the heating from room temperature to a temperature above the YBCO peritectic temperature (T_p), we surprisingly find that the YBCO thin film with a MgO substrate can be substantially superheated above the T_p of the YBCO oxide (at least 50 °C) at a heating rate of 5 °C min^{-1}. This is a novel superheating phenomenon involved in a peritectic reaction and an oxide material, which is different from one reported in systems of metals and their alloys. After the melting process, x-ray diffraction analysis was performed, which shows that Y_2BaCuO_5 (Y211) grains are in good alignment on the MgO substrate. The superheating mechanism of the YBCO oxide is discussed.

1. Introduction

In the previous work, it was found that a $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (NdBCO) thick film could grow on the $YBa_2Cu_3O_{7-\delta}$ (YBCO or Y123) thin-film-deposited MgO substrate by liquid phase epitaxy (LPE) [1, 2]. As a hetero-epitaxial growth, this YBCO-seeded NdBCO growth (YSNG) is very promising since it may be extended to the wide application field of YBCO-seeded $RE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (REBCO, RE = rare earth elements) growth. This means that the YSNG method may suit all REBCO systems, and even other perovskite ones, such as ferroelectric materials. The interesting point is that YBCO as a hetero-seed material has a peritectic temperature lower than the processing temperature of the LPE-grown NdBCO thick film. This behaviour seems to be opposite to what occurs in a common melting process.

Melting is a universal phenomenon in nature, and is also an important phase transformation in the fields of material science and condensed-matter physics. The melting of solids has been a subject of many theoretical and experimental investigations for a long time [3–6]. Much experimental evidence has shown that the melting point of a freestanding ultra-fine particle can be much depressed compared to the equilibrium melting point (T_0) of the bulk materials. However, when the particles are coated by (or embedded in) a high-T_0 solid with proper

Table 1. The heating process of the YBCO thin film.

Heating rate ($°C\,min^{-1}$)	Limit ($°C$)	Holding time (min)
80	960	5
5	1010	3
5	1020	3
5	1050	3
5	1060	3

low-energy particle/matrix interfaces (a coherent or semi-coherent particle/matrix interface), their thermal stability against melting will be enhanced, so that the melting point can be even higher than T_0. As an important finding, in 1986, the superheating phenomenon was first reported by Daeges *et al* [8] in Ag particles coated by the Au system. In this system, Ag particles can be superheated up to 25 K above T_0 for 1 min without melting. Since then, the superheating phenomenon has been observed in a number of low-T_0 metals, such as In, Pb, Cd and Tl embedded in Al or Pb in Zn and Cu, and high-T_0 metals like Ag embedded in Ni [7–13]. Almost all reported systems were limited to the metal or its alloy materials. The YBCO superconductor is an oxide material, which involves in a distinctive melting; Y123 decomposes into two phases of an Y_2BaCuO_5 (Y211) solid phase and a Ba–Cu–O (BCO) liquid phase. The formation of the new solid phase Y211 induces a surface energy. In addition, in the YSNG process, the YBCO thin-film seed layer has a semi-coherent relation with the MgO single-crystal substrate. All the above-mentioned features in the YBCO thin-film/MgO structure are absolutely related to the YSNG process. To our knowledge, no one has studied the melting mechanism of YBCO thin film on MgO substrate. In this paper, we report such a study. The objective of the present study is to extend the understanding of the melting mechanism of the oxide materials and to clarify the possible origin of YSNG.

2. Experimental details

YBCO thin film deposited on MgO substrates by the pulsed laser deposition (PLD) technique was used in this work. These films are highly *c*-axis oriented and present a 0° relationship: $\langle 100 \rangle_{YBCO} \parallel \langle 100 \rangle_{MgO}$. The YBCO thin film on the MgO substrate with a thickness of 100 nm was cut to about 1.5 mm long, 1.5 mm wide. The whole process was observed by high-temperature optical microscope (Olympus BX51M) with a heating stage (TS 1500). The temperature range is from ambient to 1500 °C, which was calibrated by 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. Firstly, the specimen was fixed onto the sapphire, which was set on the bottom of the heating furnace, then heated from room temperature to 1060 °C, which is higher than the peritectic temperature ($\sim$1010 °C) of YBCO [1]. All experiments were carried out in air atmosphere. The heating process with different heating rates was divided into several stages, as shown in table 1.

Because of the very bad thermal conduction performance of YBCO crystals, the low heating rate after reaching 960 °C and holding at certain points were used in order to assure that there is enough time to conduct heat and the displayed temperature is consistent with the real temperature of the thin film. The sample was heated to 1060 °C, held there for 3 min, and then cooled down to room temperature at a high rate.

After the melting process, the orientation relationship between the MgO substrate and the Y211 crystal was analysed by x-ray diffraction (XRD) using Cr Kα radiation.
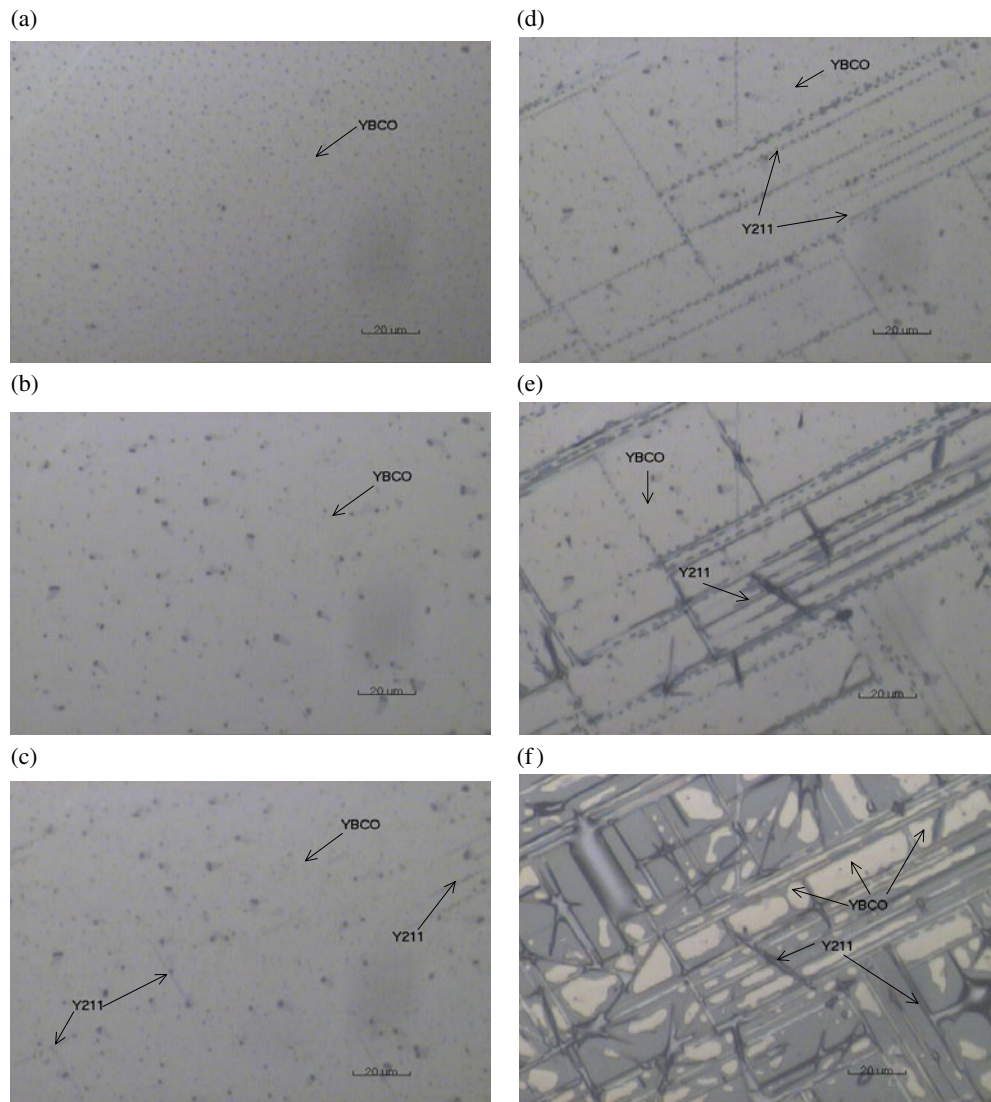
(a)

(d)

(b)

(e)

(c)

(f)

Figure 1. An optical microscope showing microstructure of a sample at (a) 960 °C for 2 min; (b) 1010 °C for 3 min; (c) 1050 °C for 0 min; (d) 1050 °C for 3 min; (e) 1060 °C for 0 min; (f) 1060 °C for 3 min;

3. Results and discussions

A series of micrographs are shown in figure 1, which illustrate an example of the observation of melting process of YBCO thin film grown on the MgO substrate.

Figure 1(a) shows an optical micrograph of YBCO thin film after holding for 2 min at 960 °C, which is below the peritectic temperature of YBCO [1]. As we can see, there were plenty of small black dots on the YBCO thin film, which were either YBCO crystal defects or impurities. It was obvious that the YBCO thin film remained almost unchanged when the sample was heated to 960 °C and held there for 2 min.

After the first heating stage, the sample was heated to $1010\,°C$, which is the peritectic temperature of YBCO [1], and held for 3 min. Figure 1(b) provides an optical micrograph of a section of sample that has been held at $1010\,°C$ for 3 min. From the figure, we can see a few changes have taken place. There were fewer black dots than in figure 1(a); meanwhile, the black dots gradually enlarged. This implies Y211 crystals nucleate and grow in these defect regions. It also indicates that melting is easily taking place in the defect regions.

Figure 1(c) gives an optical micrograph of the YBCO thin film when the temperature reaches $1050\,°C$. It was remarkable that some needle-shaped Y_2BaCuO_5 (Y211) grains gradually appeared from the undersurface, but only a small amount of YBCO thin film was melting at this temperature, which is far higher than the peritectic temperature of YBCO. This means there exists a YBCO-thin-film superheating phenomenon. Y211 grains were well aligned on the MgO substrate. The orientation may present a relationship $\langle 001 \rangle_{Y211} \parallel \langle 110 \rangle_{MgO}$. It indicates that the peritectic reaction of YBCO has partially taken place under such conditions. It is a novel superheating phenomenon of oxide superconducting materials.

When heated to $1050\,°C$, the YBCO thin film was held there for 3 min. It can be seen from figure 1(d) that there were more Y211 grains on the MgO substrate than in figure 1(c) after holding for 3 min. Needle-shaped Y211 grains with the c-axis in the long length direction were well aligned on the MgO substrate except for a very few. But the majority of the YBCO thin film was undecomposed although it endured a high processing temperature. However, on the basis of the classical theory, once melting occurs the superheating can hardly be maintained.

Figure 1(e) shows an optical micrograph of YBCO thin film when the temperature reaches $1060\,°C$. We can observe a great many well aligned Y211 grains on the MgO substrate. Y211 grains continuously grew and became thicker at the expense of YBCO crystals with an increase in temperature. This means that the melting of YBCO proceeded at this temperature.

The morphology of the YBCO thin film after holding for 3 min at $1060\,°C$ is shown in figure 1(f). Y211 crystals continued to nucleate and grew. As a result, fewer YBCO crystals were found in certain locations where Y211 grains were dense. BaCuO melts were the products of the YBCO decomposition, and covered Y211 grains due to its high wettability to Y211 and relatively low wettability to the MgO substrate. Lastly and most importantly, the undecomposed YBCO particles were still clearly visible, and unexpectedly retained between some Y211 particles, especially between two Y211 grains, especially when they have a long separation. It can be concluded that some YBCO particles can even be superheated up to $1060\,°C$.

After the melting process, the sample was analysed by XRD in order to gain the orientation relationship between the MgO substrate and the Y211 crystal. Figure 2 shows the pole figure analysis for the Y211 crystal. Here we set $\beta = 0°$ parallel to $\langle 110 \rangle$ of the MgO substrate. It can be clearly seen that the $\langle 001 \rangle$ direction of the Y211 grains orients in a $0°$ relationship to the $\langle 110 \rangle$ direction of the MgO substrate, which indicates the good alignment of most of the Y211 grains on the MgO substrate. In order to explain this phenomenon, the bonding energy between the Y211 grains and the MgO substrate crystal is considered; the bonding energy between the Y211 grains and the MgO substrate strongly depends on the lattice matching. As we know, the lattice constants of MgO are $a = b = 0.421\,12$ nm, while the lattice constant of Y211 is $c = 0.565\,93$ nm, so it agrees well with the result of XRD analysis via calculating the constants of MgO and Y211.

The melting temperature of the freestanding two-dimensional (2D) thin film is depressed compared to the bulk melting temperature according to experimental observations [14] and thermodynamic analysis [15], which is similar to the melting of nanoparticles. Though large numbers of superheating phenomena in confined nanoparticle systems are observed, superheating of a 2D thin film is rarely seen because effective suppression of melt nucleation
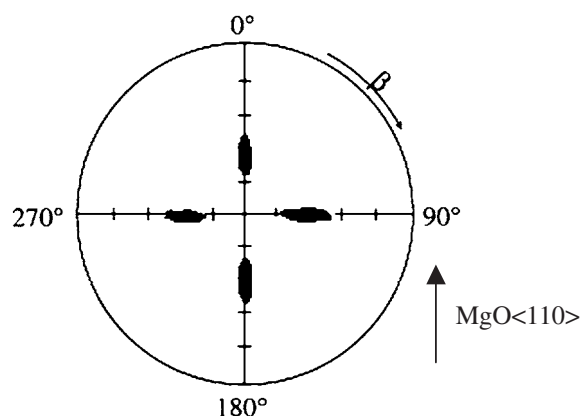
Figure 2. X-ray pole figure of the Y211 crystal on the MgO substrate.

by the epitaxial interfaces does not exist in a 2D thin film. However, recently, Zhang *et al* [16] reported the superheating of a confined thin film for the first time. In the experiment, Pb thin films with a thickness of about 20 nm were sandwiched by Al layers (about 40 nm thick). An *in situ* XRD analysis of the Pb/Al thin-film sample heated to above the melting temperature of Pb, 327.4 °C, clearly showed that a confined Pb thin film can be superheated to 334 °C. Such a superheating phenomenon in confined thin films was reasonable due to the suppression of growth of the molten droplet by the epitaxial Al/Pb/Al confinement. Another example of superheating of 2D layers on a foreign substrate is the Pb/Cu metal layer/metal substrate system [17]. The reason for this unusual effect is obviously the low dimensionality of the system and the strong influence of the substrate surface potential. The strong compression of 3.2% in the Pb layer on Cu(111) leads to an enormous increase of the melting point, more than 200 K higher than that of bulk Pb. Due to the desorption of Pb out of the first layer during annealing, the melting temperature of the compressed layer was measured by depositing additional Pb on a Cu(111) substrate [17]. On the other hand, less dense phases have lower melting point, such as the $c(2 \times 2)$–Pb/Cu(110) system [18]. But in our superheating case, the above-mentioned models are not applicable because the YBCO thin film has only one confined interface with the MgO substrate, i.e. there also exists a free surface and compression does not exist in the YBCO thin film. To explain the superheating phenomenon of the YBCO thin film, three factors have been mainly considered in our analyses. Firstly, the semi-coherent interface between the MgO substrate and the YBCO thin film is a crucial factor. Because of the good lattice match between the Y123 crystal and the MgO substrate, this interface is a low-energy interface and is favourable to suppress the heterogeneous nucleation in the interface, which would result in the superheating of the YBCO thin film. Secondly, we consider the lattice constants of Y123 and Y211 crystals. For Y211 $a = 0.7319$ nm, $b = 1.218\,02$ nm and $c = 0.565\,93$ nm, while for Y123 $a = 0.383\,36$ nm, $b = 0.388\,07$ nm and $c = 1.173\,55$ nm [19]. From the lattice match point of view, the interface between Y123 and Y211 is considerably unstable, which suppresses the occurrence of melt in the free surface or in the grain boundaries. Lastly, according to the XRD analysis, the pole figure shows that almost all the Y211 grains are well aligned on the MgO substrate due to the lattice match, so a low-energy interface is formed between them, which makes it favourable for Y211 to nucleate in this interface. At last, when the sample is superheated to a certain extent, the semi-coherent interface between the Y123 and the MgO substrate is destroyed and melting happens in the interface, which means the

peritectic melting of YBCO has started. With the peritectic reaction processing, we can see Y211 grains grow larger and emerge from the YBCO thin film, as described formerly.

4. Conclusion

By using high-temperature optical microscopy (Olympus BX51M) with a heating stage (LK 1500), the melting process of a YBCO thin film deposited on an MgO substrate is clearly observed. The orientation relationship between the Y211 crystal and the MgO substrate was gained by XRD analysis. The important finding in this study is that there exists a novel superheating phenomenon. Unlike the previously reported superheating in metallic systems, the oxide superconducting materials incorporating a peritectic melting reaction are involved. This finding leads to a conclusion that superheating exists not only in metal but also in oxide materials. In short, this work enhances our understanding of the superheating mechanism.

Acknowledgments

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