Substrate Effect on Thermal Stability of Superconductor Thin Films in the Peritectic Melting

Y. Y. Chen,[†] T. F. Fang,[†] S. B. Yan,[†] X. Yao,*[,†,‡] and B. W. Tao[§]

[†]Key Laboratory of Artificial Structures & Quantum Control (Ministry of Education) and [‡]State Key Laboratory for Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

[§]State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

ABSTRACT: Systematic experiments were performed by in situ observation of the $YBa_2Cu_3O_z$ (Y123 or YBCO) melting. Remarkably, the superheating phenomenon was identified to exist in all commonly used YBCO thin films, that is, films deposited on MgO, $LaAlO_3$ (LAO), and $SrTiO_3$ (STO) substrates, suggesting a universal superheating mode of the YBCO film. Distinctively, YBCO/LAO films were found to possess the highest level of superheating, over 100 K, mainly attributed to the lattice match effect of LAO substrate, that is, its superior lattice fit with Y123 delaying the Y123 dissolving and inferior lattice matching with Y_2BaCuO_5 (Y211) delaying the Y211 nucleation. Moreover, strong dependence of the thermal stability on the substrate material for Y123 films was also found to be associated with the substrate wettability by the liquid and the potential element doping from the substrate. Most importantly, the understanding of the superheating behavior is widely valid for more film/substrate constructions that have the same nature as the YBCO film/substrate.
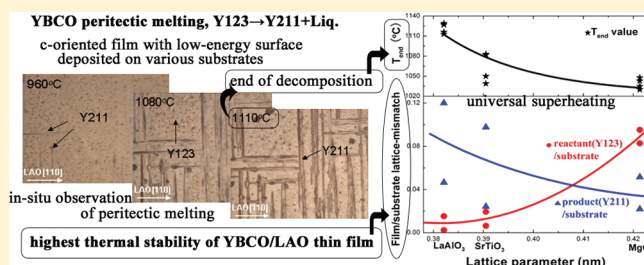
1. INTRODUCTION

The thermal stability, an intrinsic property of solid materials, is of critical concern for fundamental studies and practical applications. Since Däeges et al. first reported a superheating phenomenon in Ag particles in 1986,[1] it became increasingly imperative to understand the mechanism of thermal stability against melting, that is, superheating. In recent years, numerous researchers have reported the superheating phenomenon in varied systems.[2−4] On the basis of their intrinsic structures, three major superheating modes can be identified among the reported studies. The first one is superheating of confined particles. To be specific, when the nanosized particles are epitaxially embedded in the material with high melting point,[1,2] the particles can survive above its melting point (T_m) with semicoherent interfaces and no exposed surface. In this case, the melting is initiated inside of the bulk interior. In other words, the heterogeneous nucleation of melting at the surface and interface can be effectively suppressed in the particle–matrix system. The second one is superheating induced by suppression of melting growth in low-dimensional confined thin films. It was reported that in the Al/Pb/Al sandwiched confinement, the wetting angle at the solid/liquid interface was less than 90°, owing to the semicoherent interfaces.[3] Thus, the melting front was hindered for growth, leading to the superheated thin film. Finally, crystals with the so-called nonmelting (NM) surfaces were observed to be superheated for several degrees.[4] Melting nucleation can be effectively delayed because of the higher nucleation barrier at low-energy surfaces.

More recently, a low-dimensional YBCO/MgO thin film was observed to have a superheating property in liquid-phase epitaxial growth of a $Nd_{1+x}Ba_{2−x}Cu_3O_{7−y}$ (NdBCO) film.[5−7] After that, various experimental results confirmed that the $RE_{1+x}Ba_{2−x}Cu_3O_{7−y}$ (REBCO, RE = rare elements) thin film can endure a high temperature above their peritectic temperature (T_p).[8,9] This superheated film material with free surface provides us new perspectives for studying the superheating mechanism. It is generally believed that this superheating phenomenon is attributed to both a low YBCO surface energy and a low YBCO/MgO boundary interlayer energy.[8,10] Also, the poor wettability of the Ba–Cu–O (BCO) liquid with both the substrate and Y123 matrix is thought to be an important factor for suppressing the melting growth. On the other hand, certain elements doping the film via diffusion from the substrate might act to enhance the peritectic reaction temperature. It was reported that T_p could be effectively raised by 20 K for the NdBCO material by Mg element doping,[11] which may be a potential reason for the high thermal stability of the YBCO/MgO film. In short, factors concluded from previous works (the interface between the film and substrate, liquid wettability on the substrate, and the doping element from the substrate) strongly suggest that substrate materials may have significant importance on the thermal stability of superconductor thin films. As a typical two-dimensional thin film structure, with a free surface and a substrate, the mechanism of the substrate

effect on the thermal stability of superconductor thin films is potentially universal for other thin film materials. In other words, a novel superheating mode was necessary to be clarified and confirmed. On the other hand, thin films with high thermal stability have great applications in seed-needed processes.[12−16] Consequently, the challenge to understand the substrate effect on the thermal stability of superconductor thin films is of significant importance.

We performed a comprehensive study of the thermal stability of YBCO thin films deposited on assorted substrates in the present work. Three commonly used substrates were chosen, MgO, LAO, and STO, because at present, these three substrates are the most popular substrates that are used to fabricate YBCO thin films. We believe that they can represent the typical YBCO film/substrate interface constructions. The experimental results using both real time observation and differential scanning calorimetry (DSC) shed light on the correlation between the substrate material and thermal stability.

2. EXPERIMENTAL SECTION

The YBCO thin films were deposited on MgO, LaAlO$_3$, and SrTiO$_3$ single-crystalline substrates by varied fabrication processes. The selected films are all c-axis-oriented with four-fold symmetry and are identified by X-ray diffraction (XRD) $\theta-2\theta$ scan measurement using Cu Kα radiation and pole figure (X-ray Φ-scan) measurement. The details of these films are summarized in Table 1. On the basis of our experimental

Table 1. Details of Various YBCO Thin Films

film	thickness (nm)	deposition method	substrate lattice constant (nm)	substrate crystal system
YBCO/ MgO	200	thermal coevaporation	0.4213	cubic
	300	magnetron sputtering		
YBCO/ LAO	200	thermal coevaporation	0.3821	cubic
	200	pulsed laser deposition		($T > 435$ °C)
YBCO/ STO	300	magnetron sputtering	0.3905	cubic
	200	pulsed laser deposition		

experience, film thicknesses varying from 100 to 300 nm have negligible influence on the thermal stability compared with other critical factors.[17] The films deposited by a mature technology of thermal co-evaporation are believed to have better crystallinity because they are commercial products prepared by the company Theva GmbH. Likewise, the other films are supposed to be good and have similar quality because each group that supplied YBCO films for this work is very skillful in thin film preparation.

The melting behaviors of these films were observed in situ via a high-temperature optical microscope (Olympus BX51M) with a heating stage (TS1500). The apparatus allows a maximum temperature of 1500 °C, which is calibrated by pure silver shavings (melting at 961 °C). During the heating process, the temperature of the sample was controlled within ±1 °C by a microcomputer and measured by a Pt/Rh thermocouple. The whole heating process, as shown in Table 2, consists of several steps with different heating rates. Because of the poor thermal conduction of the substrates, the temperature was held at several fixed points for 3 min. It was confirmed to

Table 2. Heating Procedure of YBCO Thin Films in HTOM Observation

heating rate (°C/min)	limit (°C)	holding time (min)
100	900	3
30	930	3
10	950	3
5	1015	3
5	1050	3
5	1090	3
5	1150	3
quenching to room temperature		

be long enough to avoid the real temperature of the films lagging behind the nominal setting. All experiments were carried out in air atmosphere. Additionally, DSC (Labsys Evo) with a sensor (S-type, RT-1600 °C) was also performed to study the melting behaviors of YBCO thin films by the SETARAM Company.

3. RESULTS AND DISCUSSIONS

Figure 1 illustrates the typical morphologies of YBCO thin films on various substrates during the melting process, which were
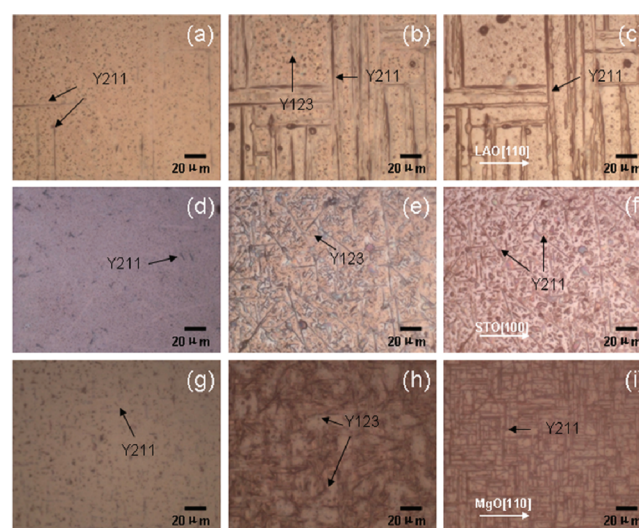

Figure 1. Morphologies of YBCO films captured during the melting process on (a) LAO at 960 °C, (b) LAO at 1080 °C, (c) LAO at 1110 °C, (d) STO at 970 °C, (e) STO at 1040 °C, (f) STO at 1060 °C, (g) MgO at 982 °C, (h) MgO at 1020 °C, and (i) MgO at 1040 °C.

captured during the in situ observation. Films deposited on different substrates show different thermal stabilities. Figure 1a−c demonstrate the evolution of the YBCO/LAO thin film at several stages. In the initial stage of melting at 960 °C, some acicular crystallites of the Y$_2$BaCuO$_5$ (Y211) phase could be seen to epitaxially grow on the film with the orientation of Y211[001]//LAO[110], indicating that the Y211 phase might nucleate from the defects or the grain boundaries on the surface. When the temperature reached 1080 °C, more Y211 grains came into view. However, the majority of the Y123 film did not decompose completely. Furthermore, the BCO liquid partially expanded on the LAO substrate, which suggests that the liquid slightly wets the substrate. Noticeably, it was not until the temperature reached 1110 °C, which is nearly 100 °C higher than the T_p of YBCO (about 1005 °C in air), that the Y123 film totally decomposed. The melting evolution strongly

confirms a high superheating capacity of over 100 K in the YBCO/LAO film, which has never been previously reported. For comparison, the melting behaviors of YBCO/STO and YBCO/MgO films are depicted in Figure 1d–f and g–i, respectively. As can be seen in Figure 1d and e, the YBCO/STO film started to melt at 970 °C and then completely decomposed when the temperature reached 1060 °C. The Y211 phase with multiple orientations simultaneously occurred on both the film surface and interface between YBCO and the STO substrate, dominating along the [110] orientation of the STO substrate. Figure 1e shows a better wettability of the STO substrate by the liquid compared with LAO. As displayed in Figure 1g–i, the YBCO/MgO film fully decomposed at 1040 °C, and the c-axis Y211 grains show an epitaxial orientation relationship with the MgO substrate, Y211[001]//MgO[110]. In addition, the liquid characteristically does not wet MgO because most liquid appears around Y211 crystals or conglobately isolated on the MgO substrate, leading to an exposed substrate shown in Figure 1h.

In short, all of these YBCO films can evidently survive at a high temperature above its T_p, suggesting a universal superheating phenomenon. However, the superheating property and the peritectic melting mode show great differences among these three films. It is noteworthy that the YBCO/LAO film has the highest superheating level among these films. Besides, the wetting behaviors of the BCO liquid on each substrate are obviously distinct from each other as well.

Apparently, the film melting starts at the temperature (T_{start}) when the Y211 phase nucleates and ends up at the temperature (T_{end}) when the Y123 film completely decomposes. Hence, the thermal stability can be compared based on these two temperatures. In order to gain reliable experimental results, more YBCO/substrates, prepared by different approaches, were used for in situ observations. The values of T_{start} and T_{end} of all samples are summarized in Figure 2. On the one hand, the
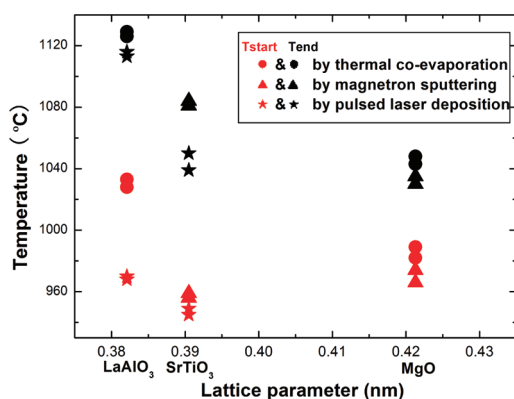

Figure 2. Summary of decomposing T_{start} (colored data at the bottom) and T_{end} (black ones at the top) temperatures of YBCO films on MgO, LAO, and STO substrates.

Y211 phase preferentially nucleates at defect sites, for example, impurities or grain boundaries, due to their high free energy.[18,19] Therefore, T_{start} is a premelting temperature that is always below T_p and is a crystallinity-dependent factor related to microstructure characteristics. For thin films with good qualities, this premelting has little effect on its stability against a complete melting. On the other hand, a complete decomposition strongly correlates the bonding energy between the film and substrate, as well as the melting mode. Thus T_{end}

represents the nature of the film/substrate construction and intrinsically indicates thermal stability of thin films. With respect to T_{start}, the relative high values of YBCO/MgO films depicted in Figure 2, owing to high quality of the films, can be attributed to the well-developed techniques in the YBCO/MgO film preparation. Besides, the discrepancy in T_{start} can be attributed to the different deposition methods, which is considered as an insignificant factor affecting the thermal stability of films in this work. Unlike T_{start}, the T_{end} values of the YBCO films on various substrates clearly display a descending order, YBCO/LAO > YBCO/STO > YBCO/MgO films, as shown in Figure 2. Remarkably, results of the YBCO/LAO films deposited by the thermal co-evaporation process show the highest T_{end} value among other films at about 1120 °C. This corresponds to a level of superheating over 100 K, a result of great interests for both fundamental study and practical applications.

We also employed DSC to study the melting behavior of YBCO thin films. A typical DSC melting trace of the YBCO/LAO film is shown in Figure 3, where two weak endothermic
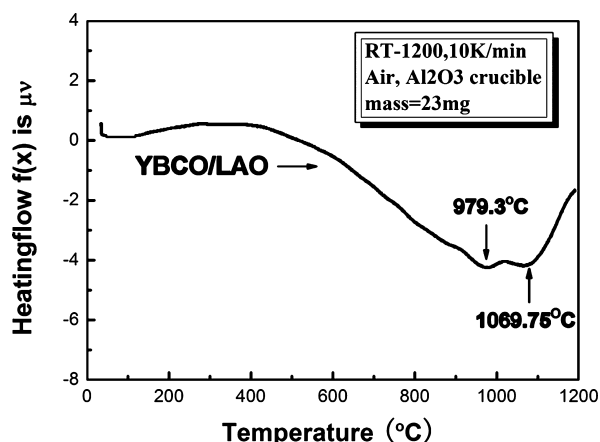

Figure 3. A typical DSC melting trace of the YBCO/LAO film in air. The heating rate of the sample is 10 °C/min. The reference sample is Al$_2$O$_3$.

peaks can be seen. As is well known, the semicoherent interface between the film and substrate can be divided into the coherent regions and defects regions. Accordingly, we suppose that the first endothermic peak around 979.3 °C implies a preferential melting of the YBCO film at the defects regions, which possesses the high free energy. On the other hand, we believe that the second one corresponds to the decomposition of the epitaxial film at coherent regions around 1069.75 °C, about 60 K above the T_p of YBCO. We interpret the DSC result as confirming a substantial superheating phenomenon of the YBCO/LAO film, which is qualitatively consistent with results from the in situ observation. However, the endothermic peaks are not so sharp and strong compared to those of conventional powder and bulk samples analyzed by DSC. Unlike the normal crystalline specimens, melting of YBCO thin films is not a transient procedure. Instead, the film melting characteristically presents a long sluggish evolution, which experienced melting nucleation at defect sites, liquid migration from the parent phase, and melting nucleation at coherent regions. This phenomenon can be attributed to the substrate effect, which will be discussed in more detail later in this paper. Moreover,

Table 3. Lattice Mismatch of Y123/Substrates and Y211/Substrates

123/sub.	Y123[100]//MgO[100]	Y123[100]//LAO[100]	Y123[100]//STO[100]	Y123[010]//MgO[010]	Y123[010]//LAO[010]	Y123[010]//STO[010]
a	0.0952	0.0024	0.0194			
b				0.0828	0.0153	0.0064
211/sub.	Y211[001]//MgO[110]	Y211[001]//LAO[110]	Y211[001]//STO[110]	Y211[010]//2MgO[110]	Y211[010]//2LAO[110]	Y211[010]//2STO[110]
b				0.0219	0.120	0.0976
c	0.0515	0.0465	0.0243			

the small thickness of the YBCO thin film should be another possible reason for the weak peaks.

On the basis of our experimental results, thermal stabilities of YBCO films (represented by T_{end}) are evidently varied with different substrates. Taking three factors into account, the substrate effect involves lattice misfit between both Y123/substrate and Y211/substrate, substrate wettability by the BCO liquid, and elements doping from the substrate.

First, as a key factor that relates to the interface bonding and energy, the lattice mismatch between the substrate and the film is considered. Basically, the large lattice mismatch will lead to dangling bonds or distortion of the crystal lattice, associated with instability sites where the melting initiates.[20,21] In the case of YBCO thin films on various substrates, the good lattice fit of Y123 on the substrate has a positive contribution to suppression of the 123 dissolving, leading to a high thermal stability of the Y123 film. On the other hand, taking the reaction of the peritectic melting into consideration, that is, Y123 → Y211+L, the weak lattice fit between Y211 and the substrate is advantageous to suppress the 211 epitaxial nucleation, which equivalently results in a high thermal stability of the Y123 film. In a word, the T_{end} strongly correlates the substrate bonding with both Y123 and Y211 at the interface. The value of lattice mismatch in this work was calculated by using the following equation

$$\text{lattice mismatch} = 2(a_1 - a_2)/(a_1 + a_2)$$

where a_1 is the lattice constant of the film material (Y123 or Y211 in this work) and a_2 denotes the lattice constant of the substrate. The lattice constants and calculated results are shown in Table 3. In addition, the substrate lattice mismatch with Y123 was calculated via the Y123(001)//substrate(100) relation because all selected films are c-axis-oriented, while the mismatch calculation of Y211/substrate is based on the epitaxial relation of Y211[001]//substrate[110] due to the growth behavior of Y211 grains observed in the melting processes. As one can see from Table 3, Y123 has the best lattice fit relationship with the LAO substrate, while the lattice mismatch between the Y211 phase and the LAO substrate is the largest one. Due to this significant feature of the LAO substrate, that is, its superior lattice fit with Y123 and inferior lattice matching with Y211, the YBCO/LAO exhibits the highest degree of superheating in comparison with other films, as demonstrated in Figure 2. In contrast, because the MgO substrate has the maximum misfit with Y123 and the minimum one with Y211, the YBCO/MgO film structure rationally has the lowest degree of superheating among others. The comparison of T_{end} shows a pronounced dependence on the lattice mismatch of films with the substrate according to our experimental results. For further discussion, in Figure 4, we summarize the correlation between the film thermal stability and the substrate lattice mismatch with the film. Both x-axes in
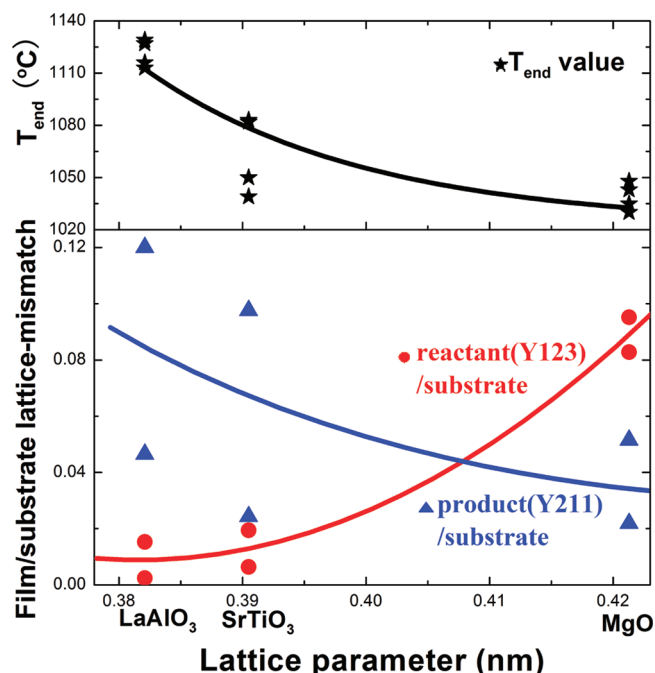

Figure 4. Correlation between the film thermal stability (T_{end} value in this work) and substrate lattice mismatch with the peritectic decomposition reactant and product, respectively (the Y123/substrate and Y211/substrate in this work).

Figure 4 denote the lattice parameter of the substrates. The y-axis in the lower part represents the film/substrate lattice mismatch, and the fitting curves for peritectic decomposition reactant Y123 and product Y211 are derived from Table 3. Comparatively, the y-axis in the upper part represents the T_{end} value of the films, and a fitting curve is gained from this work, as shown in Figure 2. Obviously, with decreasing the lattice mismatch between the substrate and peritectic reactant (Y123 in this work), the film thermal stability, namely, the T_{end} value, is strengthened. On the other hand, the superheating property of the film increases with enlarging the lattice fit between the substrate and product of peritectic decomposition (Y211 in this work). This relationship provides a novel criterion for comparing the thermal stability of films that possess a peritectic decomposition on a low-energy free surface.

Second, the wetting behavior of the liquid from film melting is considered to be an important factor. As is well known, in the case of the metal and its alloy, the liquid immediately covers the solid as long as the melting occurs, which facilitates the melting growth. However, in the melting mode of YBCO film structures in this work, the liquid from film melting correlates with the parent phase 123 and the substrate. In the present circumstance of YBCO films on varied substrates, though the liquid wetting behaviors with the 123 phases should be the same, the

wettability of each substrate by the liquid presents dissimilarity, showing a descending order, STO > LAO > MgO, as demonstrated in Figure 1. This result agrees well with the reported observation from the dipping experiment.[22] In principle, the poor substrate wettability by the BCO liquid will give rise to a liquid migration from the melting front,[8] which suppresses the melting growth because a continuous driving force for melting nucleation is required, associated with a higher T_{end}. On the other hand, the better wettability of the substrate by the liquid may accelerate decomposition of the Y123 film, leading to low thermal stability. The YBCO/STO film shows a poorer thermal stability (T_{end}) than the YBCO/LAO film, as shown in Figure 2, which agrees with the wetting behaviors. Nevertheless, the experimental results also show an incoherent relation with the substrate wettability. T_{end} of the YBCO/MgO film was minimal compared with that of other films, although MgO has the poorest wettability by the liquid. The distinction in the thermal stability of various YBCO films can not be well-explained only by substrate wettability. In brief, the substrate wettability plays an important part in the thermal stability but does not critically determine the superheating property of YBCO thin films.

Finally, apart from the main superheating related concepts discussed above, that is, interface bonding of the film/substrate and substrate wettability by the liquid, the substrate effect should be also associated with the potential doping from the substrate element. An enhancement of T_p up to 20 K for NdBCO material by Mg was reported.[11,23] In our current study, the YBCO films may have some impurity from the substrate because of the element diffusion during the thin film fabrication process. These impurities can be regarded as a kind of element doping. The doping from the substrate such as Mg and La elements may be advantageous for the superheating property of films, while with Al and Ti doping, the peritectic temperature of YBCO seems to be unaffected. According to Goodlin et al., with an impurity level up to 5% Al from the Al_2O_3 crucible and 0.5% TiO_2 from the Y_2O_3 crucible,[24] the REBCO material was believed to have an unchanged T_p. In contrast, the T_p of YBCO was identified to be slightly reduced in the Sr-doped YBCO system. According to our experimental results, the YBCO/LAO film has a better thermal stability compared with the YBCO/STO film, which seems to be in agreement with the element doping effect. However, the YBCO/STO film shows a higher degree of superheating than the YBCO/MgO film, which is contrary to the doping effect. Accordingly, we can conclude that the element doping from the substrate may have a potential effect on the thermal stability of thin films but not be a main factor. As a result, the superheating phenomenon of YBCO thin films in this work is believed to be a substantial one.

To sum up, a universal superheating mode on the basis of YBCO/substrate construction was strongly confirmed in this work. Further, the distinctions of the superheating property were clarified by substrate effects in three aspects, that is, lattice mismatch, substrate wettability, and element doping. Obviously, this mode is broadly valid for more thin film materials that have the same nature as the YBCO/substrate. More concretely, first, the film is an anisotropic material in thermal stability with a low surface energy on its exposed crystalline plane. Second, the film material possesses a peritectic melting property. Third, the substrate is excellent with the film and poor with the high-temperature phase (the product from the peritectic melting) in lattice fit. Finally, the decomposed liquid has poor wettability for both the film and substrate.

4. CONCLUSIONS

In summary, by using an in situ observation and DSC measurement of YBCO film melting, we present experimental evidence of a universal superheating mode. In particular, higher thermal stabilities of YBCO films on LAO and STO substrates than that on a YBCO/MgO film were first observed by real time investigation. Specifically, the YBCO/LAO thin film was found to have a conspicuous superheating degree over 100 K, which is of great scientific and practical interest. In particular, the crucial issue that controls the thermal stability is the lattice fit of Y123/substrate and Y211/substrate, associated with chemical bonding and free energy at the interface. Incorporating lattice fit between the film and substrate, BCO liquid behavior on the substrate, and the potential effect of element doping from the substrate, the superheating phenomenon of various YBCO films is comprehensively clarified.

This work provides a semiquantitative understanding of the relationship between substrate materials and the thermal stability of YBCO thin films, which is essential for fundamental study of thin films resembling the nature of the YBCO/substrate structure.

■ AUTHOR INFORMATION

Corresponding Author
*Tel. +86-21-54745772. Fax. +86-21-54745772. E-mail: xyao@sjtu.edu.cn.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Däeges, J.; Gleiter, H.; Perepezko, J. H. *Phys. Lett. A* **1986**, *119*, 79.
(2) Sheng, H. W.; Ren, G.; Peng, L. M.; Hu, Z. Q.; Lu, K. *Philos. Mag. Lett.* **1996**, *6*, 417.
(3) Zhang, L.; Jin, Z. H.; Zhang, L. H.; Sui, M. L.; Lu, K. *Phys. Rev. Lett.* **2000**, *85*, 1484−7.
(4) Pluis, B.; Denier van der Gon, A. W.; Frenke, J. W. M.; van der Veen, J. F. *Phys. Rev. Lett.* **1987**, *5*, 2678.
(5) Yao, X.; Nomura, K.; Nakamura, Y.; Izumi, T.; Shiohara, Y. *J. Cryst. Growth* **2002**, *234*, 611−5.
(6) Yao, X.; Nomura, K.; Huang, D. X.; Izumi, T.; Hobara, N.; Nakamura, Y.; Shiohara, Y. *Physica C* **2002**, *378−381*, 1209−21.
(7) Huang, D. X.; Yao, X.; Nomura, K.; Wu, Y.; Nakamura, Y.; et al. *J. Mater. Res.* **2002**, *17*, 747−753.
(8) Hu, J.; Yao, X.; Rao, Q. L. *J. Phys.: Condens. Matter* **2003**, *15*, 7149−54.
(9) Sun, L. J.; Tang, C. Y.; Yao, X.; Jiang, Y. *Physica C* **2007**, *460−462*, 1339−1340.
(10) Wang, Y.; Rafailovich, M.; Sokolov, J.; Gersappe, D.; Araki, T.; et al. *Phys. Rev. Lett.* **2006**, *96*, 028303.
(11) Iida, K.; Badu, N. H.; Shi, Y.; Matthew, L. S.; Miyazaki, T.; et al. *Physica C* **2007**, *463−465*, 340−343.
(12) Cai, C.; Fujimoto, H. *J. Mater. Res.* **2000**, *15*, 1742.

(13) Tang, C. Y.; Yao, X.; Hu, J.; Rao, Q. L.; Li, Y. R.; et al. *Supercond. Sci. Technol.* **2005**, *18*, L31−L34.

(14) Oda, M.; Yao, X.; Shiohara, Y.; Ikuta, H. *Supercond. Sci. Technol.* **2009**, *22*, 075012.

(15) Muralidhar, M.; Tomita, M.; Suzuki, K.; Jirsa, M.; Fukumoto, Y.; Ishihara, A. *Supercond. Sci. Technol.* **2010**, *23*, 045033.

(16) Muralidhar, M.; Suzuki, K.; Ishihara, A.; Jirsa, M.; Fukumoto, Y.; Tomita, M. *Supercond. Sci. Technol.* **2010**, *23*, 124003.

(17) Tang, C. Y.; Cai, Y. Q.; Yao, X.; Rao, Q. L.; Tao, B. W.; et al. *J. Phys.: Condens. Matter* **2007**, *19*, 076203.

(18) Alsayed, A. M.; Islam, M. F.; Zhang, J.; Collongs, P. J.; Yodh, A. G. *Science* **2005**, *309*, 1207.

(19) Pusey, P. N. *Science* **2005**, *309*, 1198.

(20) Zhu, D. M.; Dash, J. G. *Phys. Rev. Lett.* **1986**, *57*, 2959.

(21) Pettersen, M. S.; Lysek, M. J.; Goodstein, D. L. *Phys. Rev. B* **1989**, *40*, 4938.

(22) Krauns, Ch.; Tagami, M.; Yamada, Y.; Nakamura, M.; Shiohara, Y. *J. Mater. Res.* **1994**, *9*, 1513−1518.

(23) Babu, N. H.; Shi, Y.; Iida, K.; Cardwell, D. A. *Nat. Mater.* **2005**, *4*, 476.

(24) Goodilin, E. A.; Shiohara, Y. Single-Crystal Growth for Science and Technology. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Ed.; Elsevier: Amsterdam, The netherlands, 2000; Vol. *30*, Chapter 189, pp 67−227.