Growth and superconducting transition of Pr$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_7$–$\delta$ ($x \approx 0.5$) epitaxial thin films

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Abstract
Pr$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_7$–$\delta$ ($x \approx 0.5$) thin films have been grown on SrTiO$_3$(STO) and yttrium-stabilized ZrO$_2$(YSZ) substrates by pulsed laser ablation. The substrate temperature dependence of orientation and superconducting properties were systematically studied. Good quality $c$-axis and $a$-axis orientated films can be obtained on SrTiO$_3$ solely by changing the substrate temperature. On YSZ, films with good $c$-axis orientation can be grown, while it is hard to grow films with good $a$-axis orientation by changing substrate temperature alone. The highest $T_C$ is about 37 K, which is found in the films grown on YSZ with a good $c$-axis orientation. For the films grown on STO, however, the highest $T_C$ is about 35.6 K, with a mixed orientation of $c$-axis and $a$-axis. In most of the superconducting films, the weak temperature dependence of the normal state resistivity, as characterized by small $R(290\text{ K})/R(50\text{ K}) \leq 2$ ratios, together with a weak localization behaviour just above $T_C$, could be attributed to the essential scattering due to the localized electronic states. The superconducting transitions in a field up to 10 T along the $c$-axis have been measured on a $c$-axis oriented film grown on SrTiO$_3$. The zero-temperature in-plane upper critical field $B_{c2}^a(0)$ is estimated from the resistivity transition data.

1. Introduction

Among the high-$T_C$ cuprates, compounds with the RBa$_2$Cu$_3$O$_{7-\delta}$ ($R$ = rare-earth elements) structure, the so-called 123 structure, have properties which are nearly independent of $R$ except for $R$ = Pr [1, 2]. Although PrBa$_2$Cu$_3$O$_{7-\delta}$ (Pr-123) can be formed, it does not show superconductivity at low temperature and even shows no metallic behaviour [3]. There are also reports on superconductivity in Pr-123 [4, 5]; however, the bulk superconductivity of Pr-123 has to be independently verified and also the structure of superconducting Pr-123 has to be confirmed by rigorous crystallography. Optical study has shown that PrBa$_2$Cu$_3$O$_{7-\delta}$ is a charge transfer type insulator with a charge-transfer gap $\Delta_{CT}$ ~ 1.4 eV, and carriers in the chain are localized at low temperatures and low frequencies [6]. Due to the depletion of mobile carriers, the in-plane electric transport properties in Pr-123 could be described in terms of variable range hopping (VRH) in the insulating region [7]. When the high-temperature cuprates are doped with Pr the superconductivity is usually suppressed [8], and often a metal–insulator transition occurs, accompanied by the presence of complicated magnetic behaviour due to the relatively large magnetic moment of Pr ions [9]. The origin of the suppression of superconductivity in high-temperature superconductors by Pr and the absence of superconductivity in Pr-123, being of fundamental interest, may also shed light on the mechanism of high-temperature superconductivity, since any reasonable theory should explain the effect of Pr on superconductivity in 123 systems.

If the carriers’ depletion were indeed the main origin for the absence of superconductivity in Pr-123, a simple
approach could be to introduce carriers by chemical doping. A substitution of divalent element such as Ca for Pr appears to be a natural choice. Nevertheless no superconductivity was found in samples with fairly low Ca doping levels (<30% at ambient pressure [10, 11]). Norton et al successfully revived superconductivity in Pr-123 epitaxial thin films by substituting 50% of the tetravalent Pr by divalent Ca [12, 13]. And later, superconductivity was again found in high-pressure synthesized Ca-doped Pr-123 bulk samples [14, 15]. However, the influence of crystal structures on superconductivity in thin films is still somewhat ambiguous. For example, it is necessary to study the superconductivity in films with different orientations systematically. And also it is important to make a comparative study of the transport properties of thin films and that of ceramic bulk samples. The transport properties of Ca-doped Pr-123 bulk samples sintered at ambient pressure have been studied by Luszczek [16]. However, researches are harassed by the limited Ca substitution levels and no superconductivity was observed, whereas, for samples synthesized at high pressures, impurity phases seem hard to be avoided, although the Ca content is highly improved [17]. In this paper, we report a systematic investigation on the substrate temperature dependence of film orientation, the superconducting transition temperature and the residual-resistivity ratio for Pr0.5Ca0.5Ba2Cu3O7−δ thin films grown on substrates of SrTiO3 (STO) and yttrium-stabilized ZrO2 (YSZ). Some LaAlO3 (LAO) and LaAlO3)$_3$(Sr$_2$AlTaO$_6$)$_{1/2}$ (LSAT) substrates were also used. A silicon heater was utilized in the film deposition, and the temperature was monitored by an infrared thermocouple with a calibrated temperature range from 300 to 1200 °C. A self-made NiCr–NiAl thermocouple was placed at the back of the heater as a temperature reference. An LPX 300 KrF (λ = 248 nm) excimer laser (Lambda Physik) was adopted for the film growth. The repetition rate was 5 Hz and the fluence was about 2 J cm$^{-2}$. The target–substrate distance was kept at 70 mm. The films were deposited in an oxygen partial pressure of 40 Pa, as frequently seen in the growth of YBCO. After deposition, a one-minute holding before annealing was used for the purpose of stress relaxation. The annealing process was carried out in 1 atm oxygen at a cooling rate around 15 °C min$^{-1}$ for about 10 min (the superconductivity of the film was found to be hardly dependent on the annealing duration in these circumstances). The films were then cooled down naturally to room temperature. The superconducting critical temperature of the films was measured using a standard four-probe technique, with the electrodes mounted by silver paste directly onto the films.

Inductively coupled plasma (ICP) results show a good consistency of the film stoichiometry with that of the target, as expected from the pulsed-laser ablation method. The orientation of the films was characterized by x-ray diffraction (XRD). On STO, films with c-axis lying in the film plane (a-axis oriented) can be obtained by a reduction of 160 °C of the substrate temperature T$_S$, as compared with that for films with c-axis perpendicular to the film surface (c-axis oriented). Typical XRD patterns for films with c-axis and a-axis orientation, grown at a temperature of 780 and 720 °C, respectively, are shown in figure 1(a) and (c), respectively. Films grown at an intermediate T$_S$ of ~ 740 °C possess a structure with mixed c-axis and a-axis oriented phases, as shown in figure 1(b). A weak (103) peak, which is the strongest line of the target spectrum, can sometimes be seen as T$_S$ was further reduced. The surface profile of the films were obtained by atomic force microscopy (AFM). The mean roughness is around 4 and 20 nm in a 10 x 10 μm$^2$ area for the a-axis and c-axis oriented films, respectively. As a comparison, the intensity ratios of (005) and (200) of the film to (200) of the substrate, varying with T$_S$, are also shown in figure 1(d). Typical resistance transitions for the films with different orientation are shown in figure 2. Here, the resistance of the films is scaled by the respective value at 290 K, R (290 K). The labels ‘c-oriented’, ‘mixed oriented’ and ‘a-oriented’ on the curves correspond to substrate temperatures of 880, 790 and 720 °C, respectively. The low-temperature part of the transition of the curves is also enlarged in the inset of figure 2 for a clearer view. It is evident that the film structure has a substantial effect on both the superconducting and normal state properties of the film. On YSZ substrates, good quality c-axis oriented films can also be obtained, as shown in figure 3. The substrate temperature in such a growth process was around 900 °C, slightly higher than that in the case of STO. It can be attributed to the 45° rotation of the R-123 unit cells on YSZ. However, it was found to be difficult to grow a-axis films on YSZ solely by varying T$_S$. When T$_S$ was reduced lower than that for a-axis oriented films grown on STO, more and more characterized peaks of the target appeared. A typical XRD pattern for the films grown at about 700 °C is shown in figure 3(b). We can see that peaks other than the (001) and (000) are shown. For substrates such as LAO and LSAT, good quality c-axis oriented films can also be obtained.

It is found that the critical temperature changes with the substrate temperature. Figure 4 shows the substrate temperature T$_S$ dependence of the critical temperature for films grown on STO. The error bars of T$_{Conset}$ and T$_{CO}$ correspond to the temperature range from 100% to 90% of ρ$_a$, and 10% to 0 (within the resolution of the instruments used) of ρ$_a$, respectively. Here ρ$_a$ is the normal state resistivity, defined as the value where the sample resistivity deviates from linear temperature dependence near the superconducting transition. The relationship of T$_C$ and T$_S$ for the films on YSZ is also shown. A higher T$_S$ is necessary to grow epitaxial thin films on YSZ than on STO, due to the larger lattice mismatch of

2. Film growth and characterization

A Pr$_{0.5}$Ca$_{0.5}$Ba$_2$Cu$_3$O$_{7-δ}$ ceramic target was prepared using a conventional solid state reaction method similar to that used to produce superconducting R-123 pellets. Stoichiometric quantities of high-purity dry Pr$_2$O$_3$, CaCO$_3$, BaCO$_3$, and CuO powders were ground, mixed, fired, pelletized and sintered several times. The sintering temperature was 900 °C. The whole process was carried out in air under an ambient pressure. Powder x-ray diffraction indicated a predominant R-123 phase while a small amount of BaCuO$_2$ could also be detected. The Pr$_{0.5}$Ca$_{0.5}$Ba$_2$Cu$_3$O$_{7-δ}$ epitaxial thin films were grown using pulsed-laser ablation mainly on substrates of SrTiO$_3$ (STO) and yttrium-stabilized ZrO$_2$ (YSZ). Some LaAlO$_3$ (LAO) and (LaAlO$_3$)$_3$(Sr$_2$AlTaO$_6$)$_{1/2}$ (LSAT) substrates were also used. A silicon heater was utilized in the film deposition, and the temperature was monitored by an infrared thermocouple with a calibrated temperature range from 300 to 1200 °C. A self-made NiCr–NiAl thermocouple was placed at the back of the heater as a temperature reference. An LPX 300 KrF (λ = 248 nm) excimer laser (Lambda Physik) was adopted for the film growth. The repetition rate was 5 Hz and the fluence was about 2 J cm$^{-2}$. The target–substrate distance was kept at 70 mm. The films were deposited in an oxygen partial pressure of 40 Pa, as frequently seen in the growth of YBCO. After deposition, a one-minute holding before annealing was used for the purpose of stress relaxation. The annealing process was carried out in 1 atm oxygen at a cooling rate around 15 °C min$^{-1}$ for about 10 min (the superconductivity of the film was found to be hardly dependent on the annealing duration in these circumstances). The films were then cooled down naturally to room temperature. The superconducting critical temperature of the films was measured using a standard four-probe technique, with the electrodes mounted by silver paste directly onto the films.

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Figure 1. Influence of the substrate temperature $T_S$ on the orientation of Pr$_{0.5}$Ca$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ thin films grown on STO. Typical XRD patterns for films grown at $T_S$ of (a) 880°C, (b) 765°C, and (c) 720°C are shown. Peaks of the substrate are marked with a postfix ‘s’. Shown in (d) is the $T_S$ dependence of the ratio $I(005)/I(200)$ and $I(200)/I(200)$, where $I(hkl)$ is the diffraction intensity of (hkl) peak for the film or the substrate.

Figure 2. Typical resistance transition of different oriented films grown on STO. The resistance of these films is normalized to the value at 290 K, i.e., $R$ (290 K). Here, the labels ‘c-oriented’, ‘mixed oriented’ and ‘a-oriented’ correspond to substrate temperatures of 880, 790 and 720°C, respectively. The inset is the low temperature part of the transition of these films.

The former. Accordingly, $T_C$ for the films on YSZ is higher, which could also be due to a larger strain at the interface. The highest $T_C$ is about 35.6 and 37 K for the films grown on STO and on YSZ, respectively. It is worth noticing that on STO, the films with higher $T_C$ are those with a structure of mixed c-axis and a-axis oriented phases, as was reported earlier by Norton et al [12]. For the films grown on YSZ, the variation tendency of the measurement data seems to suggest a better superconductivity for the c-axis oriented films than for those with a-axis orientation.

An interesting thing about the films is their metastable properties. As the solubility of Ca in the bulk materials sintered at ambient pressure is less than 30%, metastable properties of the target with higher Ca doping levels could be expected, as having been pointed out by Norton et al [13]. Sintering the bulk materials under high pressure can raise the Ca substitution level to 70%. Superconductivity exhibits in bulks with Ca doping level from 30% to 70%, as mentioned previously in the literature [17]. However, the superconducting bulk materials became insulating after being fired in a furnace in air at a temperature higher than 200°C for half an hour [18]. Comparatively, by real-time monitoring using the reflection high energy electron diffraction (RHEED) system, we found that it took less than 1 min for the film diffraction pattern to vanish, when the film was placed in a background pressure $10^{-4}$ Pa at a temperature higher than 200°C. There is nothing but some spots, which can be observed by the naked eye, remaining on the substrate after such a heating process. The spots are found to be insulating (the resistance read from a multimeter is of the magnitude of MΩ).
3. Superconducting transition in a magnetic field

The in-plane resistance measurement was carried out using the standard four-probe method on one of the c-axis oriented films grown on STO. The thickness of the film was around 800 Å. The current density used was 700 A cm$^{-2}$. Low ohmic contacts were made to the sample by coating the electrodes with Pt, and using silver paste to attach gold lines firmly to the electrodes.

A part of the $R$–$T$ curve measured at zero field is shown in the inset of figure 5(a). The critical temperature $T_{\text{conset}}$ is about 47 K, with a transition width of about 6 K (from 90% to 10% of $\rho_\infty$), which is close to other reports [12, 13, 19]. However, the film has a smaller resistivity just above $T_C$, $\rho(T_{\text{conset}}) = 357 \, \mu\Omega \text{cm}$. From the graph we can see that the transport behaviour is metallic at high temperatures, but at temperatures just above $T_C$, the resistance has a very small enhancement. This should not be a contribution from the resistance along c-axis direction, since in the film any a-axis oriented phase can be fully ruled out according to the XRD data. We would rather attribute the effective enhancement to some kind of weak localizations, although at present we do not have enough evidence to determine what kind of localization it is. We propose that in the film there are some localized charge carriers, so the small enhancement is the combined result of the free carriers’ itinerating and the localized carriers’ variable range hopping.

Superconducting transitions of the film in a field of 0.5, 1, 2, 4, 6, 8, and 10 T are presented in figure 5(a). For a more clear inspection, we plot the $H$–$T$ phase diagram of the film in figure 5(b) using the criteria 1%, 10%, 50%, 90%, and 99% of $\rho_\infty$ respectively. Line 1 is very close to the irreversible line and line 5 is very close to the upper critical field.

4. Discussions

A common feature in the film transport behaviour is that the in-plane resistivity ratio $R (290 \, \text{K})/R (50 \, \text{K})$ is less than 2 (more precisely is 1.6) for the films grown on both STO and YSZ, as indicated by the hollow stars in figure 4. Before the superconducting transition, the resistivity of these films rises slightly, suggesting a weak carrier localization. The small resistivity slope and the localization-like behaviour near the superconducting transition temperature, which are often observed in 50% Pr doped YBCO, are almost independent of the magnetic field strength, as being noticed from the resistivity data at $B \leq 10$ T. The weak localization behaviour could be attributed mainly to the low carrier density, as having been
to suggest an occurrence of a structural defect dependent delocalization of the carrier.

We have made an estimate about the upper critical field $B_{c2}$ from the field-dependent superconducting transition measurements. By using the criteria of the 99% and 90% of the normal-state resistivity $\rho_n$ for the determination of $B_{c2}$, a linear temperature dependence is obtained near $T_{\text{Conset}}$ with a slope $dB_{c2}/dT$ estimated to be around 3.5 and 1.73 K T$^{-1}$ for line 1 and line 2 respectively, as seen in figure 5(b). Using the Werthamer, Helfand, and Hohenberg (WHH) [22] extrapolation to low temperatures with $B_{c2}(0) = 0.73(-dB_{c2}/dT|_{T=0})T_c$, the zero-temperature in-plane upper critical field is estimated to be $B_{c2}^{ab}(0) \simeq 105.5$ T for line 1 and $B_{c2}^{ab}(0) \simeq 47.1$ T for line 2.

5. Summary

We have grown Pr$_{1-x}$Ca$_x$Ba$_2$Cu$_{3-x}$O$_y$ epitaxial thin films on different substrates using the pulsed laser ablation technique. Good quality $a$-axis and $c$-axis oriented films can both be obtained on STO by varying the substrate temperature. On YSZ, films with good $c$-axis orientation have also been grown. The highest $T_C$ is around 35.6 and 37 K for films grown on STO and YSZ substrates, respectively. These are consistent with the results of superconductivity in Ca-doped Pr-123 as reported by Norton et al. previously. The films show a metastable thermostability. The very small $R$ (290 K)/$R$ (50 K) ratio together with the localization and a large normal state resistivity of the films is perhaps caused by the essential scattering due to the localized electronic states. The superconducting transitions in a magnetic field up to 10 T for one film grown on STO have been measured. The zero-temperature in-plane upper critical field $B_{c2}^{ab}(0)$ is also estimated from the resistance data.

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