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Anisotropic properties of the high-quality epitaxial $YBa_2Cu_3O_{7-\delta}(110)$ thin film

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High-quality ($T_c \sim 86$ K and phase purity > 99%) epitaxial $YBa_2Cu_3O_{7-\delta}(110)$ thin films have been obtained by inverted-cylindrical-magnetron-sputtering deposition on a single crystal (110) $SrTiO_3$ substrate. A unique feature of this film is the in-plane alignment of the c axis of the $YBa_2Cu_3O_{7-\delta}$ film in a single direction, which is very important for the study of the anisotropy in this material. The crystal orientation of the film has been investigated using x-ray diffraction to collect pole figures. Our resistivity and optical-reflectivity measurements have revealed pronounced anisotropic behavior.

The layered structure is common to all cuprate superconductors. The two dimensionality associated with this layered structure has been manifested in an interesting anisotropic behavior in the electronic, magnetic, thermal, optical, and even mechanical properties of these materials. The study of this intrinsic property is crucial to the understanding of the superconductivity mechanism and to the device application of the high-T_c superconductors. However, knowledge of these important issues is limited. Even the anisotropy in the transport properties of $YBa_2Cu_3O_{7-\delta}$ is still ambiguous. The ratio of the normal-state resistivity along the c axis and ab plane has been reported with different values ranging from 30 to 300 by different groups.[1-5] The temperature dependence of the normal-state resistivity in $YBa_2Cu_3O_{7-\delta}$ is controversial. Both metallic[1-3] and nonmetallic[4,5] behaviors have been observed along the c direction. The largest difficulty in the investigation of anisotropy is the lack of a single-crystalline thin-film sample. It should be pointed out that all these anisotropy measurements to date have been made on single-crystal bulk samples, not on thin films. Conceptually, anisotropy measurements should be easier to perform on thin films. However, the highest-quality epitaxial c- or a-oriented films available are still not good enough for such a study. TEM (Refs. 6 and 7) pictures of these films have indicated that microstructures with perpendicular in-plane orientation, usually 20–100 nm in size, distribute evenly in the film so that it is difficult to obtain information on the anisotropy of these films.

We have recently overcome such a difficulty by growing high-quality (110) orientation $YBa_2Cu_3O_{7-\delta}$ film on a (110) $SrTiO_3$ substrate, and then studied the anisotropy of such a film. In this paper, we report the growth of these films and the characterization including anisotropy studies of normal resistivity and light polarization.

The growth of the single-crystal $YBa_2Cu_3O_{7-\delta}$ thin film requires the careful selection of two major parameters: substrate and deposition condition. It is well known that $YBa_2Cu_3O_{7-\delta}$ has an orthorhombic crystal structure. The ideal substrate for the single-crystal $YBa_2Cu_3O_{7-\delta}$ thin film should have close lattice constants and be orthorhombic. Unfortunately, most substrates currently being used for growing epitaxial thin films, such as (100) MgO and $SrTiO_3$, have two identical in-plane lattice constants. $LaAlO_3$ is orthorhombic at low temperature but is not twin free. Therefore when $YBa_2Cu_3O_{7-\delta}$ is deposited on these substrates, small grains of perpendicular orientation, which are microscopic compared to the sample dimension, will be nucleated to maintain the two orthogonally mixed states in the macroscopic scale. The grain size may depend on the lattice mismatch, deposition condition, and surface condition of the substrate, but grains of different orientations are almost inevitable and their volume portions are about the same as each other.

Recently, we have been able to make *in situ* high-quality a-oriented $YBa_2Cu_3O_{7-\delta}$ films[8] on single-crystal (100) $SrTiO_3$ and $LaAlO_3$ substrates by using the inverted cylindrical magnetron sputtering technique.[9] The fact that both c-oriented and a-oriented films can be selectively grown on the same substrate implies that the orientation of the $YBa_2Cu_3O_{7-\delta}$ thin film is actually a competition resulting from the coincidence of the substrate lattice constants and the three axes of $YBa_2Cu_3O_{7-\delta}$ or, more precisely, two axes because during deposition $YBa_2Cu_3O_{7-\delta}$ is tetragonal. The competition can be controlled by the deposition temperature T_s and the oxygen partial pressure P_{O_2}.[10,11] Under certain P_{O_2}, there exist optimum deposition temperatures T_{sa} and T_{sc} for the a-oriented and c-oriented films. In our system, T_{sa} is about 680 °C–710 °C and T_{sc} is 40 °C–80 °C higher. When $T_s \leq T_{sa}$, the lattice mismatch between the c axis with $LaAlO_3$, $SrTiO_3$, and MgO is the smallest among all three axes of $YBa_2Cu_3O_{7-\delta}$. Therefore the c axis will preferentially lie down on the substrate surface with the a-axis standing up. As T_c increases, the thermal expansion of the c axis grows very fast[10] and then more and more of the c-oriented nucleation centers will be generated and finally become dominant at T_{sc}. Therefore, with an orthorhombic substrate and proper control of the deposition condition, it is possible to grow single-crystal $YBa_2Cu_3O_{7-\delta}$ thin films of different orientations.

Single-crystal $SrTiO_3$ has been one of the best substrates for the growth of $YBa_2Cu_3O_{7-\delta}$ thin film especially due to the high perfection of the film orientation. Even though it has cubic crystalline structure, its (110) plane is orthorhombic. The mismatch of its in-plane (100) axis and $YBa_2Cu_3O_{7-\delta}$ c axis is 0.2% while its (110) axis has the mismatch 10 times larger. Similar to the competition between the c and a orientations on the (100) $SrTiO_3$ substrate, there is also a competition between the (110) and

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(103) or (013) phases. Under the deposition conditions which favor the *a*-oriented film, the *c* axis of $YBa_2Cu_3O_{7-\delta}$ will preferentially align with (100) so that (110) phase will dominate. Growing $YBa_2Cu_3O_{7-\delta}(110)$ film has been attempted previously,[11–13] but only mixed (110)/(013) films or (110) films with low T_c and a rough surface have been obtained.

The sputtering atmosphere is composed of a mixture of 170 mTorr Ar and 130 mTorr O_2 gases. The partial pressure of the oxygen P_{O_2} plays an important role in the film's composition. Based on the Rutherford-back-scattering-spectrometry and x-ray analysis, higher P_{O_2} will result in a copper oxide phase and low P_{O_2} will induce Y-rich composition. In both cases, the T_c is more or less depressed. The substrate is mechanically clamped to the heating block at 705 °C during the deposition. In order to achieve a constant thermal contact, we clean the heating surface each time before mounting the substrate. The reproducibility of good films is considerably high. The deposition temperature is controlled by a thermocouple clamped to the heating block like the substrate. A higher deposition temperature T_s will induce the (013) phase, while lower T_s can result in a low T_c. The plasma current was held at 580–600 mA and the gap voltage was about 120–115 V during the deposition. The deposition rate is about 40 Å/min and the final film thickness is about 2500–3500 Å. After the deposition, the film is quickly cooled to 510 °C in 10-Torr oxygen atmosphere and annealed at this temperature for half an hour in one atmosphere oxygen.

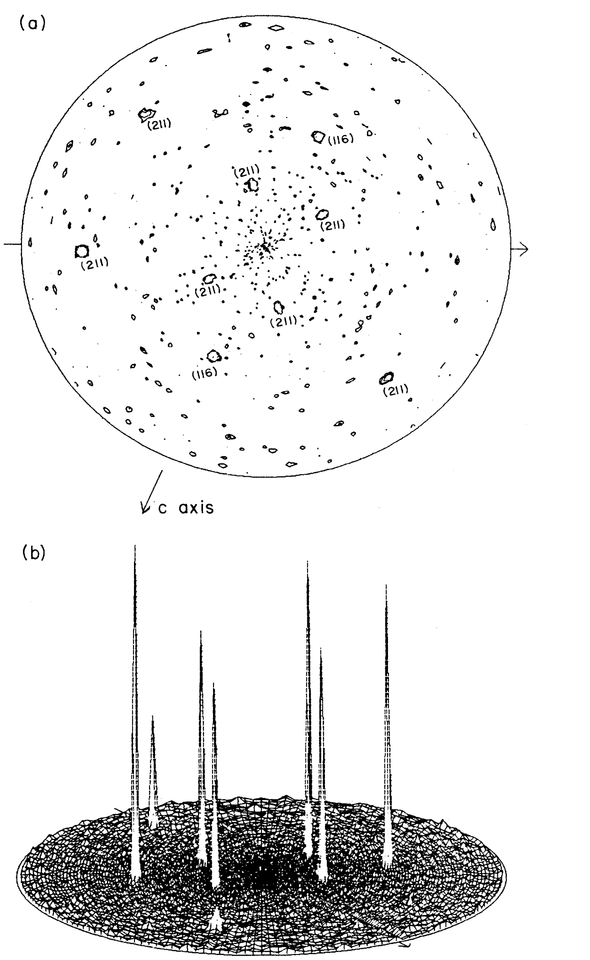

FIG. 1. X-ray-diffraction pole figure of (116) peaks. (a) The planar view—small islands are the projection of the peaks and the tiny dots are the background noise; (b) pole intensity in arbitrary unit.

Figure 1 shows the (116) pole figure obtained using a Siemens D5000 x-ray diffractometer equipped with an open Eulerian cradle. Neglecting the background noise, we have seen the sharp (116) peaks from the film and the (211) peaks from the substrate. It has been noticed that the two (116) peaks are 180° apart and the straight line connecting them, which represents the *c* axis of the film, coincides with the (001) axis of the substrate as we predicted. Since the (116) peaks from $YBa_2Cu_3O_{7-\delta}(103)$ phase locate closely to the substrate's (211) peaks, we cannot rule out the possibility of the (110)/(103) mixture in our film by only Fig. 1. In order to investigate quantitatively the phase purity of the film, we have checked the ϕ scan of (108) peaks from (110) (at $\chi=76°$) and (103) (at $\chi=24°$) oriented phases, respectively [Figs. 2(a) and 2(b)] using the same counting time and scanning speed. Figure 2 is the (108) ϕ scan on one of our best films. The intensity of the (108) peaks from (110) phase are, on average, around 130–150 while the (108) peaks from the (103) phase are almost invisible (< 10). By multiplying a χ angle correcting factor ($\sim$5.5 from Si) to their intensities, we can roughly estimate the ratio of the (110) and (103) phases by

$$(110)\% = \frac{I^{(108)}_{(110)} \times 5.5}{I^{(108)}_{(110)} \times 5.5 + I^{(108)}_{(103)}} . \qquad (1)$$

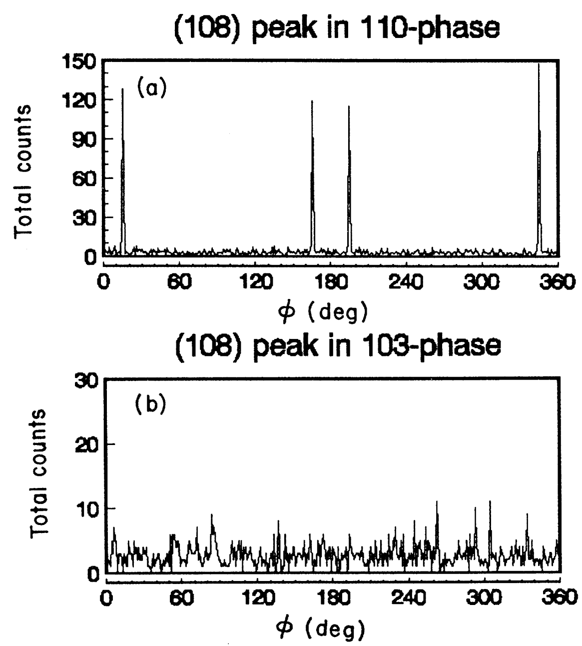

FIG. 2. (108) ϕ scan for (a) the (110) phase and (b) the (103) phase, respectively.

Generally, the purity of the resulting (110) film is above 90% and the best (Fig. 2) is greater than 99% pure. Before doing all these calculations, we also checked the $\theta - 2\theta$ scan to rule out the existence of other phases except the (110) and (103) phases. We may not be able to identify the a and b axes for the (110) film, but the c axis and the ab plane are well separated.

The surface of our (110) films looks very shiny and smooth. The scanning-electron-microscopy picture does not show any features down to the scale of 300 Å. Near-normal incidence optical-reflectivity measurements performed on the (110) thin-film samples reveal the anisotropic nature of the two axes in the surface plane. As can be seen in Fig. 3(a), light with E parallel to the c axis (at the positions 20° and 200°, respectively, due to the zero offset) has a much lower reflectivity than light with E parallel to the ab plane (at 110° and 290°). This relationship is valid for all wavelengths of light studied [Fig. 3(b)]. While the ratio of $R_c/R_{(110)}$ is not constant for all wavelength, R_c is always smaller than $R_{(110)}$. This property is to be expected due to the metallic nature of the ab plane and the semiconductorlike behavior along the c axis. Others have obtained similar results using light in the mid-ir range.[13] Due to the limited range of wavelengths examined, using the Kramers-Kronig relations to determine the dielectric constants would be of little use; however, even in this limited range, the anisotropic nature of the (110) thin films is evident.

By using the photolithography and wet-etching methods, the films were patterned into five radial lines [Fig. 4(a)] for the regular four probe measurement. The lines are 1.5 mm long and 20 μm wide. The angle θ between line 1 and line i ($i=2$, 3, 4, and 5) are 25°, 43°, 63°, and 90°, respectively. Line 1 is parallel to the c-axis, therefore line 5 is along the ab plane. The resistivity versus temperature curves of these five lines have been measured using linear LR-400 resistance bridge and

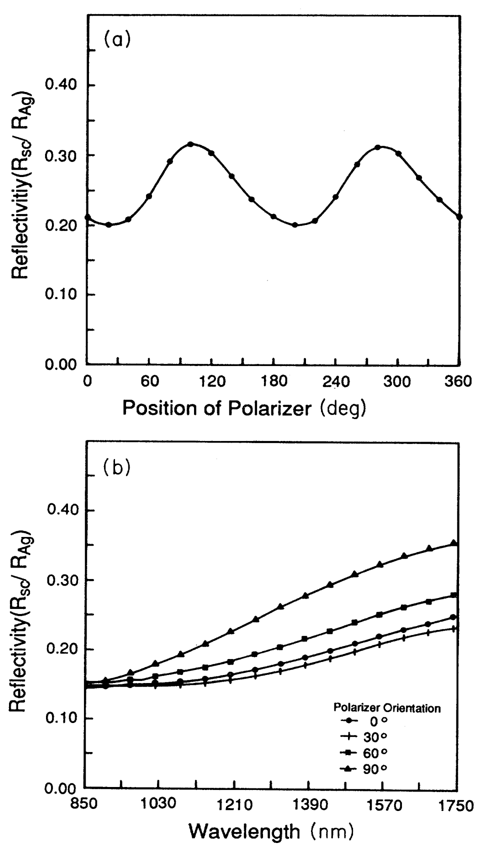

FIG. 3. (a) Reflectivity vs polarization for the wavelength equal to 1500 nm. (b) Reflectivity vs wavelength. Four polarizations of light were used.

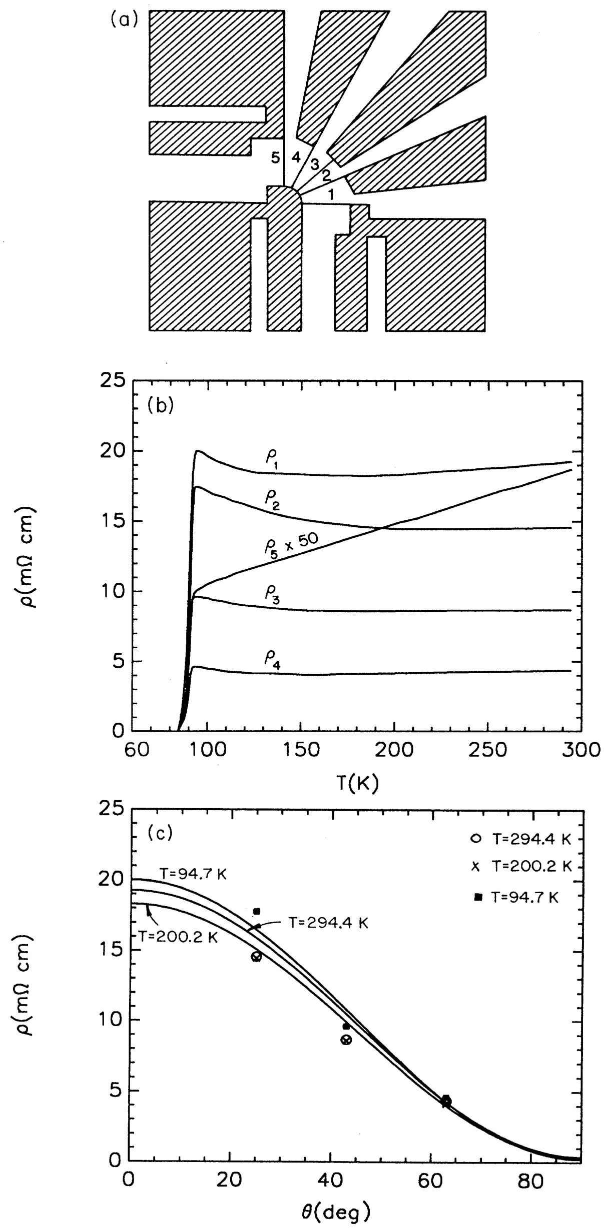

FIG. 4. (a) The five line pattern for the resistivity anisotropy measurement on the (110) film. (b) Temperature dependence of the resistivity of lines 1–5 on the (110) film. (c) Comparison of the measured $\rho(\theta)$ with the theoretical calculation.

Au/chromel thermocouple. The results are shown in Fig. 4(b) with the scale of line 5 magnified 50 times. It is clear that all five lines have $T_c = 84.5$ K. However, in the normal state, ρ and its T dependence differ from lines 1-5. First of all, resistivity increases monotonically as the direction of the line approaches the c axis from the ab plane. Considering the orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$, we may write the resistivity along θ direction as follows:

$$\rho(\theta) = \rho_{ab}\cos^2\theta + \rho_c \sin^2\theta , \qquad (2)$$

where ρ_c and ρ_{ab} are the resistivity along the c axis and (110) axis, respectively. Figure 4(c) shows a comparison between the theoretical and the experimental results. The solid lines are calculated from Eq. (1) with (ρ_{ab}, ρ_c) being taken from the experimental data as (0.374, 19.25), (0.296, 18.29), and (0.202, 20.0) in unit of (mΩ cm) at $T = 294.4$, 200.2, and 94.65 K, respectively. It has been noticed that the normal-state resistivity of these five lines fit Eq. (2) approximately from room temperature to T_c. In our thin-film samples, ρ_c/ρ_{ab} is found to be $\sim$30–50 at room temperature and the anisotropy becomes stronger ($\sim$100 at 94.65 K) with decreasing temperature. This is consistent with the same measurement on the single-crystal bulk sample.[1] Second, there is a change of $d\rho/dT$ from metallic to semiconductorlike as θ increases. ρ in line 5 (ρ_{ab}) decreases monotonically from room temperature to T_c. As θ increases, the ρ vs T curves become flatter at the low temperature and curve up as T approaches T_c, which implies the semiconductorlike behavior is already dominant. The three samples used in this experiment each showed a similar behavior in the resistivity measurement. We have also measured some films with lower (110) phase purity and found the anisotropy in the resistivity is dramatically smoothed when the film contains 5% (103) phase and it no longer exists at 10%. All lines in these low-purity samples show metallic behavior. It has been reported that ρ_c is very sensitive to the oxygen content of $YBa_2Cu_3O_{7-\delta}$ so that a slight oxygen deficiency[3] would change its T dependence. The observation of the upturn in the ρ_c vs T curves of our 86 K film sample further indicated that the oxygen deficiency which degrades T_c from 92 to 86 K may be more than enough to induce this metal-nonmetal transition. In order to understand the significance of this property, more experiments, such as the temperature and the field dependence of the I-V curve along the ab plane and c axis are being investigated.[14] The resistivity measurement is also a confirmation that our films are pure (110) phase. Otherwise, the semiconductorlike T dependence of the resistivity will be shorted out and only metallic behavior could be observed as in the a-oriented films.[6]

In summary, high-quality $YBa_2Cu_3O_{7-\delta}$(110) films with $t_c \sim 86$ K have been reproducibly fabricated by the inverted-cylindrical-magnetron-sputtering technique on single-crystal (110) $SrTiO_3$. The in-plane alignment of the $YBa_2Cu_3O_{7-\delta}$ c axis in a single direction has been confirmed by x-ray pole figures. The optical-reflectivity and the resistivity measurement have shown strong anisotropy between the c axis and the ab plane. This anisotropy, plus the large coherence length along (110) direction of the film, will have potential device applications.

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