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Anisotropic electronic structure of in-plane aligned *a*-axis $YBa_2Cu_3O_{7-\delta}$ thin films

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Polarization-dependent x-ray absorption near-edge spectra (XANES) of the O 1*s* has been measured on a highly in-plane aligned *a*-axis $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin film. The in-plane XANES, with the electric field *E* of the linearly polarized synchrotron light being parallel to the *b* or *c* axis of YBCO films ($E//b$ or $E//c$) were obtained in a normal-incidence alignment. The XANES for $E//a$ was then calculated from the data obtained by varying the angle. The results lend strong support to those obtained by using detwinned YBCO single crystals in all crystalline orientations, including the extrapolated *c*-axis spectra. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1590057]

Determination of the exact location and concentration of the hole and its symmetry in the high-temperature superconductors (HTSCs) has attracted tremendous attention because it has been generally conceived as a key to understand the origin of superconductivity. For many years, the electronic structure of CuO_2 planes and CuO_3 chains and the distribution of holes on all oxygen and copper sites in single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) have been extensively investigated by using polarization-dependent x-ray absorption near-edge spectra (XANES) of the O 1*s* and Cu 2*p*.[1–4] It is, however, difficult to handle a small size single crystal and precisely reproduce the light spot on the sample to exclude the dependence of the incident photon energy.[2] A natural alternative is to use YBCO thin films for such investigations. The usual (001) YBCO films nonetheless often contain significant twins, making it difficult to resolve the intrinsic properties along respective crystalline orientation. Instead, only average XANES for the electric field *E* of the polarized light parallel to the *ab* plane of the (001) films ($E//ab$) was obtained.[5]

Well in-plane aligned (100) and (110) oriented YBCO thin films provide us the opportunity to fabricate different types of planar sandwish-type Josephson junctions[6,7] as well as to investigate the anisotropic properties of HTSC, such as transport properties,[8] *d*-wave symmetry of the superconducting gap,[9] ultrafast dynamics of carrier relaxation,[10] and electronic structure. Here we report the results of polarization-dependent XANES experiments using a highly in-plane aligned *a*-axis YBCO thin film. The in-plane XANES ($E//c$ and $E//b$) were obtained in a normal-incidence alignment. Furthermore, the XANES for $E//a$ was extrapolated from data obtained with different oblique incidence angles. Therefore, the XANES for the three polarizations $E//a$, $E//b$, and $E//c$ are unambiguously distinguished.

It has been suggested that a PBCO buffer layer can facilitate the *a*-axis YBCO nucleation[11] on K_2NiF_4 type (100) $LaSrGaO_4$ (LSGO) substrates.[12] However, due to the low substrate temperature required to form the *b*-axis PBCO layer, the YBCO films obtained all suffered from significant degradation in T_c. Here we present a modified deposition process, which produces well-aligned *a*-axis YBCO films. The energy density and the repetition rate of the 248 nm KrF excimer laser pulse were 3 J/cm^2 and 5 Hz, respectively. In our process, a 50-nm-thick PBCO template was deposited on a LSGO substrate at 660 °C and in 0.1 Torr O_2. Then, without interrupting PBCO deposition, the substrate temperature was raised at a rate of 20 °C/min until it reached 780 °C. The target was then switched to YBCO and the oxygen pressure was raised to 0.28 Torr immediately. Finally, a 300-nm-thick YBCO was deposited on the PBCO template. After the deposition, the film was cooled in 600 Torr of oxygen to room temperature with the heater off.

The resistivity versus temperature characteristics of the *a*-axis films was determined by a standard four-probe method and is shown in Fig. 1(a). The transition temperatures along *b* and *c* axes were 91.1 and 88.7 K, respectively. The crystallinity of the films was analyzed by measuring the x-ray diffraction (XRD) pattern, the full width at half maximum (FWHM) of the rocking curve of the (200) peak, and the x-ray Φ scanning. As shown in Fig. 1(b), the XRD patterns

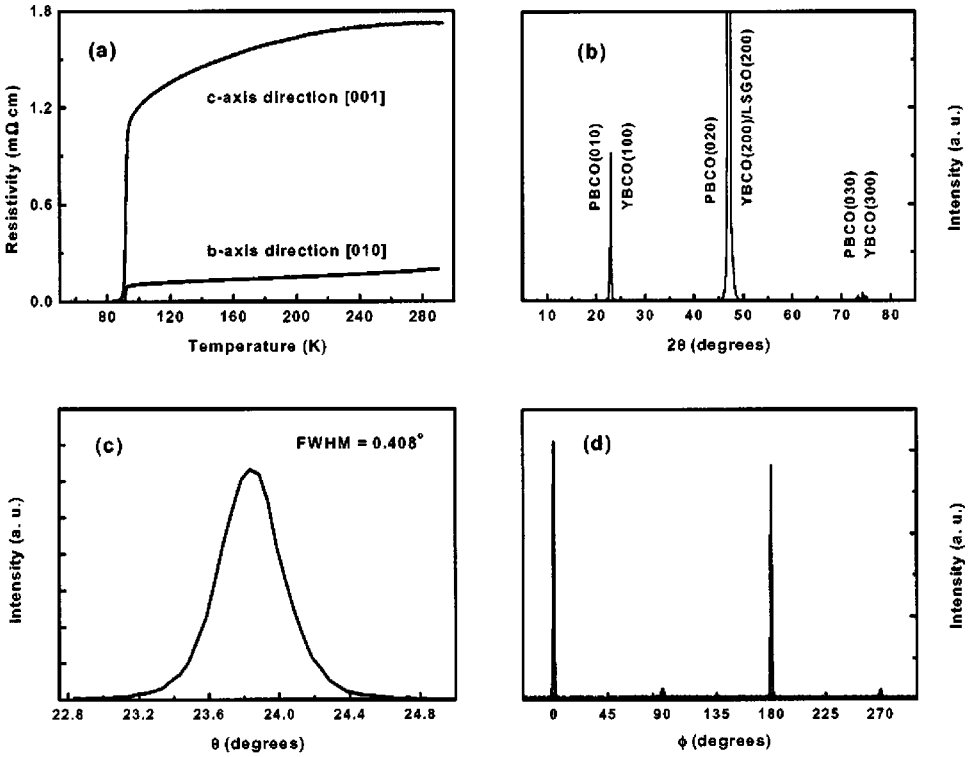

FIG. 1. (a) The temperature dependence of in-plane resistivity; (b) the x-ray diffraction pattern; (c) the FWHM of the rocking curve of the (200) peak; and (d) the Φ scanning in the (102) plane of the *a*-axis YBCO thin film deposited on $LaSrGaO_4$ substrates.

of the films were essentially *a*-axis oriented and no peaks other than the (100) peaks were observed. The FWHM of the rocking curve of the (200) peak is shown in Fig. 1(c) and was less than 0.41°. The degree of in-plane alignment, as revealed by x-ray Φ scanning in the (102) plane [Fig. 1(c)], was better than 97%.

The *a*-axis YBCO thin film was cut into two equivalent pieces and rotated 90° with respect to each other for aligning the *E* field of the linear-polarized x ray to the *b* and *c* axes of YBCO. The whole arrangement is depicted schematically in Fig. 2. The linearly polarized x ray (523–618 eV) was supplied by a 6 m high-energy spherical monochromatic beam line at Synchrotron Radiation Research Center, Hsinchu, Taiwan, Republic of China.[13] Because the polarization state in the cross section of the monochromatic beam are linear at center and circular at both sides, the 95% linear polarization was achieved by using the narrow slits centered on the orbital plane. The energy resolution of the monochromator was set to be 0.1 eV at O 1*s* absorption edge. The flurorescence light was detected at an angle of 45° with respect to the incident beam using a microchannel plate detector.[14] Shifts in the energy for the monochromatic light were calibrated using the known Cu 2*p* absorption peak of the CuO compound. The incident photon number (I_0) was measured simultaneously by a gold mesh located behind the exit slit of the monochromator and calibrated by the flurorescence-yield measurements of a clean gold film mounted on the sample holder. All measurements were normalized to I_0.

In order to compare the absorption cross sections at different O sites, the O 1*s* absorption spectra recorded up to 618 eV were calibrated by the self-absorption effect.[15] In the energy range $591\,\text{eV} \leqq E \leqq 618\,\text{eV}$, the spectra are almost struc-

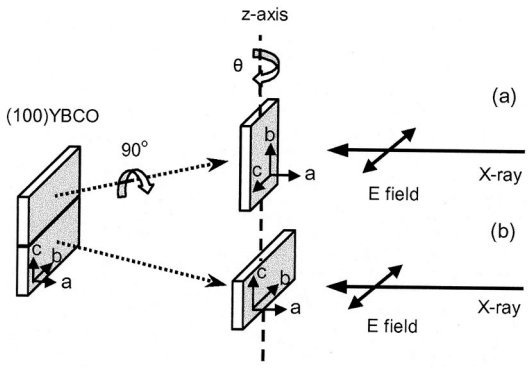

FIG. 2. Schematics of the experimental setup of polarization-dependent XANES. The electric field *E* of the linear-polarized x ray is parallel to the (a) *c* or (b) *b* axis of an in-plane aligned *a*-axis YBCO thin film.

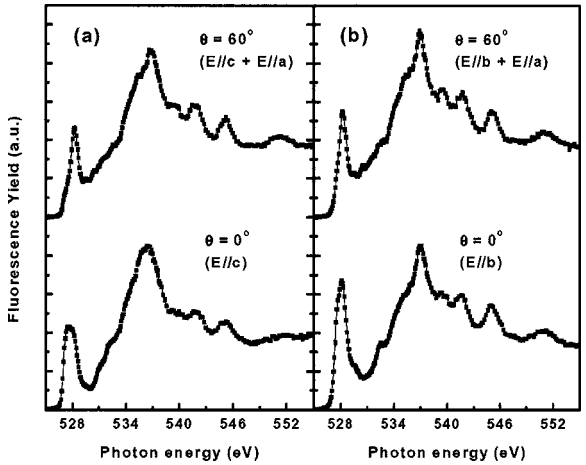

FIG. 3. The XANES in (a) and (b) are the results of Figs. 1(a) and 1(b), respectively.

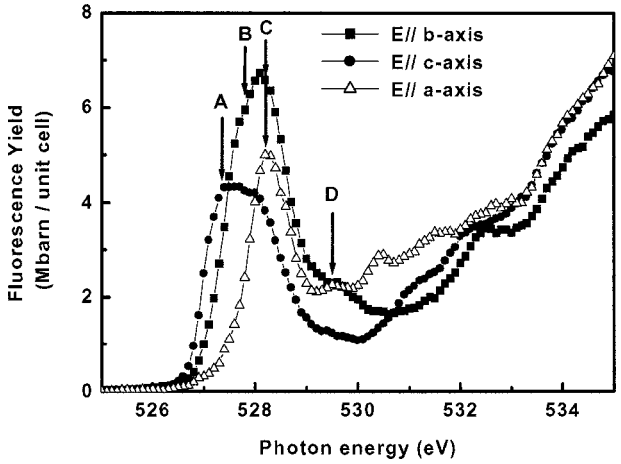

FIG. 4. Comparison of the O 1*s* XANES of in-plane aligned *a*-axis oriented YBCO thin films for polarization $E//a$, $E//b$, and $E//c$ axes. peak *A*: 527.5 eV, peak *B*: 527.8 eV, peak *C*: 528.3 eV, and peak *D*: 529.5 eV.

tureless and hence they could be normalized to the tabulated standard absorption cross section.[16]

For the case of normal incidence ($\theta=0°$), the $E//b$ or $E//c$ absorption spectra can be obtained by rotating the (100) YBCO films such that *b* or *c* axis of the film is parallel to *E*. The O 1*s* in-plane XANES for $E//c$ and $E//b$ are shown in Figs. 3(a) and 3(b), respectively. In addition, the absorption spectra for the oblique incidence at $\theta=60°$ were obtained by rotating the sample along the vertical (*z*) axis, as shown in Figs. 3(a) and 3(b). Consequently, the O 1*s* XANES along the *a* axis could be calculated from $I_\theta = I_0\cos^2(\theta)+I_{90}\sin^2(\theta)$, where I_0, I_{90}, and I_θ are the fluorescence yield at the incident angles $\theta=0°$ ($E//b$ or $E//c$), $\theta=90°$ ($E//a$), and $\theta=60°$ ($E//a+E//b$ or $E//c$), respectively. Therefore, the XANES for the three polarizations $E//a$, $E//b$, and $E//c$ are distinguishable as shown in Fig. 4.[17]

The high-energy part, above 532 eV of XANES, is due mainly to continuum absorption to Y 4*d*, 4*f*, and Ba 4*f* empty states hybridized with O 2*p* states[12] and displays a similar feature for all cases. The pre-edge ($E<532$ eV) absorption spectra, on the other hand, exhibits very different features among various axes. These results are consistent with those obtained by using twin-free YBCO single crystals reported by Nücker *et al.*[2] The absorption peak *A* for $E//c$ at 527.5 eV is caused by the core-level excitation of the O 1*s* electron to both O $2p_z$ orbitals associated with the apical O(4) atoms. For $E//a$ and $E//b$, the main pre-edge absorption peaks (peak *C*) occur at almost the same energy, $\sim$528.3 eV. This state is due to the strong hybridization between Cu $3d_{x^2-y^2}$ and O $2p_{x,y}$ orbitals, which leads to the formation of the local singlet state, called the ''Zhang–Rice'' singlet.[18] From the band structure calculation of $YBa_2Cu_3O_7$, [19] the contribution of O(2) and O(3) in the CuO_2 planes to the spectra of $E//a$ and $E//b$ should be about the same. Hence, the shoulder on the low-energy side (peak *B*, $\sim$527.8 eV) of the main absorption peak for $E//b$ is believed to arise from the unoccupied density of states of one O(1) site in CuO_3 chains, which is absent for $E//a$. This implies that the binding energy of O(1)1*s* is inbetween those of O(4) and O(2,3). In addition, the peak *D* at 529.5 eV can be assigned to transition into unoccupied O 2*p* states admixed to the upper Hubbard band. Thus, it is only observable in the spectra for $E//a$ and $E//b$.

In summary, we have demonstrated that the O 1*s* XANES along *a*, *b*, and *c* axes is obtained from the in-plane aligned (100) oriented YBCO thin films. These spectra are consistent with the results obtained from the detwinned single crystal. Since one can estimate the hole distribution on each oxygen site by the curve-fitting analysis, the current results suggest that many fundamental aspects of high-T_c cuprates could be resolved by studying the doping and temperature dependent XANES using in-plane aligned *a*-axis thin films. Measurements along the line are in progress and will be reported separately.[9,10]

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