

Characterization by X-Ray Diffraction of Non-*c*-Axis Epitaxial $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Thin Films

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Abstract—Thin films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) with the non-*c*-axis (117) orientation were grown by MOCVD on (110) LaAlO_3 single crystal substrate. XRD $\theta - 2\theta$ scans show that films contain also (119) and (011)Bi-2212 impurity grains. We propose and report characterization of the non-*c*-axis films by XRD $\varphi - \psi$ scans. By this approach, the assumed theoretical film-substrate relationship of the (117) Bi-2212 grains is demonstrated experimentally. The result also confirms twinning in the span rooflike (117) Bi-2212 grains. The impurity (119) and (011) Bi-2212 grains are also rooflike and *in-plane* aligned according to film-substrate relation and AFM images so that the film can be considered *in-plane* epitaxial.

Index Terms—MOCVD, thin film, XRD $\varphi - \psi$ scans, (117)Bi₂Sr₂CaCu₂O₈.

I. INTRODUCTION

HIGH Temperature Superconductors (HTS) are intrinsic composite structures composed of superconducting and non-superconducting layers. Anisotropy of the properties is high. The coherence length in the *ab*-plane is about 5–300 times greater than that along the *c*-axis. For some intrinsic Josephson tunneling devices, the non *c*-axis HTS thin films may offer the advantage of exploitation of a longer coherence length than for typical *c*-axis films. Furthermore, in HTS the coherence length along the *c*-axis ($\xi_c \sim 0.01$ – 0.2 nm) is quite small when compared to classic superconductors such as Nb ($\xi \sim 40$ nm). This situation makes at present challenging fabrication of multilayered Josephson tunneling devices based on HTS *c*-axis oriented thin films. Namely, the non superconducting layers should have the thickness small, i.e. comparable to the coherence length along the *c*-axis of the HTS. On the other hand, integration of non *c*-axis thin films combining HTS with other materials can lead to design of new and complex heterostructures for fabrication of devices with improved or

new functionality taking advantage of the synergetic effects at interfaces. Therefore, growth of top quality non *c*-axis thin films and heterostructures [1]–[5] can be rewarding.

It was demonstrated that Bi-based (Bi-Sr-Ca-Cu-O) superconductors exhibit the intrinsic Josephson junction (IJJ) effect [6], [7]. The IJJ effect was also observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ [8], [9]. The Bi-based superconductor is more suitable for device applications because of its higher anisotropy parameter. Using Bi-based superconducting single crystals, various methods of IJJ fabrication have been developed and different IJJ device prototypes have been reported [9]–[12]. For Bi-based thin films, usually *c*-axis oriented growth is easily obtained. For such a case, the IJJ effect was demonstrated by fabricating a mesa structure [13]. Despite this success, for some device applications a higher number of junctions defined by the stacked alternative superconducting and insulating layers of the crystal structure are required. This translates into a higher thickness of the *c*-axis film and this has some limitation considering the decrease of the film quality for thick films. To overcome the addressed limitation of the *c*-axis films, it would be of practical interest to grown non *c*-axis films and to design IJJ devices using such films.

In our previous works [5 and therein refs] we have grown different non *c*-axis HTS thin films or heterostructures. Superconducting layer was of $\text{YBa}_2\text{Cu}_3\text{O}_7$ or $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. In this work we report growth of a non *c*-axis epitaxial (117) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) thin films on appropriate (110) LaAlO_3 (LAO) single crystal substrate. We show characterization of these films by XRD $\varphi - \psi$ scans. This proposed approach applied on (117) Bi-2212 films has the potential to be used for structural characterization of other non *c*-axis films. The result of the XRD $\varphi - \psi$ scans experimentally demonstrates the assumed film-substrate relationship according to the lattice coincidence theory. It also supports the idea of twin formation in the specific roof-like grains from the non *c*-axis films. It is worthy to mention that we have recently reported high critical current densities in (001)Bi-2212 thin films grown by MOCVD in which we observed defects such as dislocations parallel to the *ab*-plane and anti-phase boundaries considered effective for strong flux pinning [14]. Assessment of other types of defects in Bi-2212 films such as twins can be of interest for the flux pinning control and better understanding of vortex dynamics details.

II. EXPERIMENTAL

Samples were prepared by metal organic chemical vapor deposition (MOCVD). Source materials (Toshima Manufacturing Co. Ltd.) were $\text{Bi}(\text{o-tolyl})_3$ and $\text{M}(\text{DPM})_2$ with $\text{M} = \text{Sr}$,

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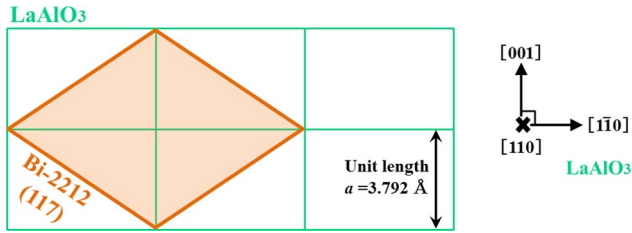


Fig. 1. Film-substrate lattice matching relationship for the growth of the non-*c*-axis (117)Bi-2212 thin film. Same *in-plane* relation is for (119)Bi-2212 impurity grains. The lattice misfits between the film and the substrate along the [001] and [110] directions of the substrate are 0.98% and 8.95%, respectively.

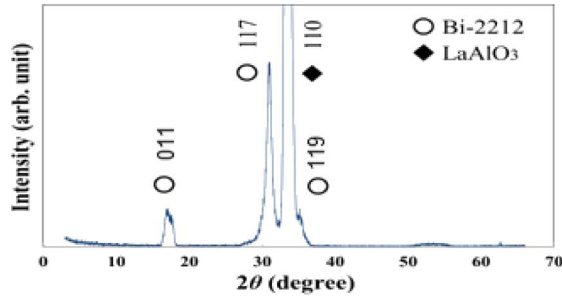


Fig. 2. XRD $\theta - 2\theta$ scan of the (117)Bi-2212 film.

Ca and Cu. DPM is the abbreviation for dipivaloylmethanate ligand. Vapors were supplied to reaction tube in Ar-carrier gas stream with the following flow rates: 100, 300, 300, and 70 ml/min for Bi, Sr, Ca and Cu, respectively. The substrate placed on a susceptor was inductively heated at 500–800 °C. The thin film presented in this work was grown at 600 °C for a deposition time of 45 h on a (110)LAO single crystal substrate produced by Furuuchi Chemical Co. The miscut angle of the as-received (110)LAO single crystal substrates, as measured by atomic force microscopy (AFM), was below 0.3°. Oxygen was introduced in the reaction tube with a partial pressure of 2.6 kPa and a flow rate of 640 ml/min. The total pressure in the chamber was 6.7 kPa. More details on equipment are presented in [15], [16]. The average film thickness was ~ 50 nm. The thickness was determined considering mass established from measurements of Inductively Coupled Plasma (ICP-AES, SPS 7700, Hitachi High-Tech Science Co.) Spectroscopy and the theoretical density of the Bi-2212 phase (6.6 g/cm³).

X-ray diffraction (XRD) measurements were performed on Ultima (Rigaku Co.) and X'Pert MRD (Panalytical Co.) diffractometers (CuK α radiation).

The morphology of the non *c*-axis films was observed by AFM using a SPA 400 (Hitachi High-Tech Science Co.) equipment.

III. RESULTS AND DISCUSSIONS

The substrate was selected to match the most probable theoretical *in-plane* relationship (Fig. 1) between the lattices of the substrate and the film.

Growth of the film with (117) orientation can be observed from the XRD $\theta - 2\theta$ pattern presented in Fig. 2. However, other diffraction lines are present and they are ascribed to (011) and (119) orientations of Bi-2212. In the case of (011) Bi-2212,

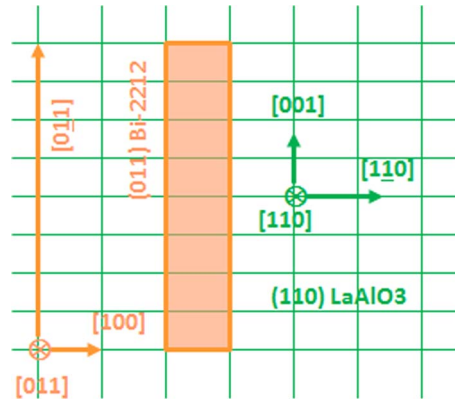


Fig. 3. Film-substrate lattice matching relationship between the (011)Bi-2212 and (110) LAO planes.

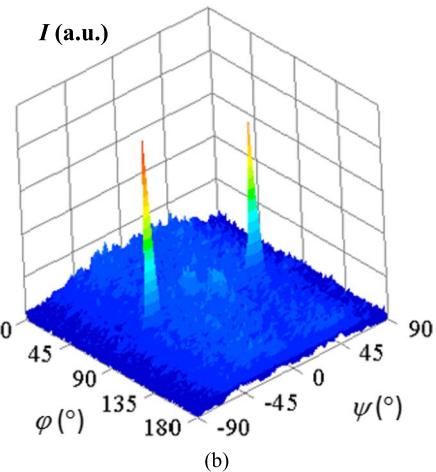
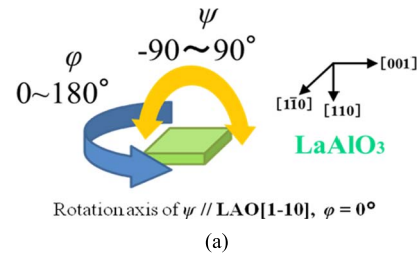


Fig. 4. XRD $\varphi - \psi$ scans of the (117)Bi-2212 film. (a) Schematic of the measurement. (b) $\varphi - \psi$ experimental results for the (0010) plane ($2\theta = 29.048^\circ$) of the non-*c*-axis Bi-2212 film.

this plane matches the (110) LAO plane as shown in Fig. 3, while for the (119) Bi-2212 it is as in Fig. 1.

The XRD $\varphi - \psi$ scans were performed for $2\theta = 29.048^\circ$ corresponding to (0010) plane of Bi-2212. For a fixed ψ within ($-85^\circ, 85^\circ$), φ -scan was measured. A schematic drawing of the measurement is shown in Fig. 4(a). The ψ -step was of 5° . Experimental results are presented in Fig. 4(b). The two observed peaks have (φ, ψ) values of ($87.5^\circ, -50^\circ$) and ($90.75^\circ, 45^\circ$). A ψ value of 45° or 50° is comparable to the theoretical values of 41.03° for (117) and 48.23° for (119) orientations of Bi-2212. The differences may arise from the contribution of the substrate miscut angle. By RHEED, Kuroda *et al.* [1] obtained an angle of about 48° in a (11n)Bi-2212 thin film. It was not possible for our resolution of the measurement to separate the

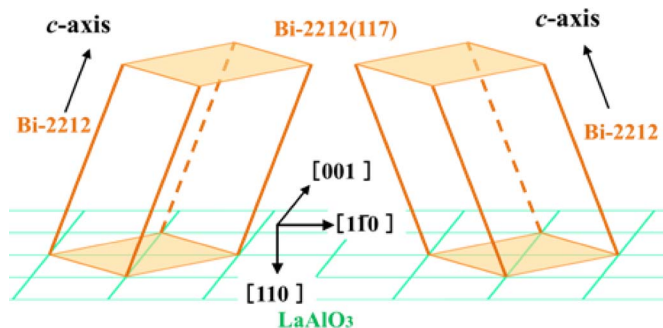


Fig. 5. Schematic image showing formation of inclined facets of the span rooflike grains containing twins.

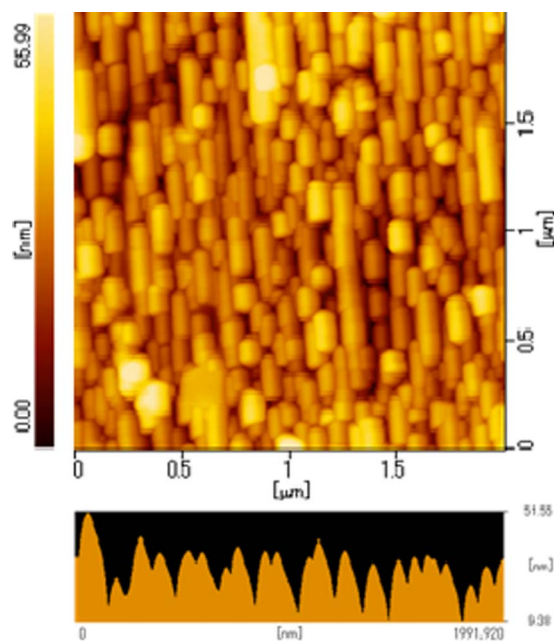


Fig. 6. AFM image and cross-section view of the span rooflike grains.

two orientations. We conclude that there is a relatively good agreement between the theoretical and experimental values within the experimental errors.

The measurement indicates that *c*-axis is inclined with the indicated ψ angles in respect to the normal to the substrate surface (Fig. 5). The non *c*-axis film grows in the *c*-axis direction by a layer-by-layer mechanism through addition of *ab*-planes similar to the growth of the *c*-axis thin film, but the *c*-axis is inclined versus the substrate surface. When the two opposite inclined growing fronts merge (Fig. 5), a span roof-like grain forms and it contains a twin boundary. Therefore, XRD $\varphi - \psi$ scan results prove the formation of twins in the non *c*-axis film.

The span roof-like morphology of the grains is revealed by AFM (Fig. 6) and it is in good agreement with the results of XRD measurement. AFM also suggests that films are *in-plane* epitaxial. The experimental value of φ at $\psi \cong 45^\circ$ close to 90° (Fig. 4(b)) and the φ experimental data for the substrate surface (not shown) indicate that the film is epitaxial for the (117) or (119) Bi-2212 grains given their similar *in-plane* film-substrate lattice matching relation (Fig. 1). From the film-substrate lattice matching relation for the (011) Bi-2212 grain (Fig. 3), the *in-plane* epitaxy of the film is preserved; the grains of

(117)/(119) accommodate the (011) Bi-2212 grains. The grains of (011) should have a roof-like morphology that is formed as already explained for the (117) or (119) Bi-2212 grains, and the top line of the roof theoretically develops perpendicular to that for the (117) or (119) Bi-2212 grains. In AFM it was not possible to identify grains with such orientation and in the $\varphi - \psi$ space (Fig. 4(b)) of the (0010) Bi-2212 plane, the corresponding peaks of (011) Bi-2212 should be located close to $\psi = \pm 90^\circ$ where measurements were not performed yet. We shall also note that for the films deposited at a higher growth temperature (i.e. above 600°C) the peak of (011) Bi-2212 in the XRD $\theta - 2\theta$ patterns cannot be observed and, hence, the formation of this impurity phase is suppressed.

IV. CONCLUSION

Non *c*-axis films of (117) Bi-2212 were obtained by MOCVD. Substrate was the (110) LAO single crystal. The film was characterized by structural and microstructural measurements and it shows *in-plane* epitaxy. The *in-plane* epitaxy for the (117) and impurity (119) Bi-2212 was demonstrated experimentally by $\varphi - \psi$ XRD scans. This confirms the assumed theoretical film-substrate lattice matching relation for the (117)/(119) Bi-2212 grains and formation of the twins in the non *c*-axis grains developing with a span roof-like morphology. XRD $\theta - 2\theta$ measurements indicate the presence of the (011) Bi-2212 impurity. This phase based on the film-substrate relation and AFM images is *in-plane* aligned preserving the overall *in-plane* epitaxy of the film.

XRD $\varphi - \psi$ scans of non *c*-axis film proposed in this work are useful for characterization of other inclined films.

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