

# Nucleation and Growth of b-Axis Oriented $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$ Thin Films on $\text{LaSrGaO}_4$ (100) Substrates

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## ABSTRACT

Good quality a-axis oriented thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  may be grown by the use of a  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$  (PBCO) layer as a template. Here we present a detailed study of the nucleation of the PBCO layer, explaining the orientations observed. It is determined that the wavy surface of a  $\text{LaSrGaO}_4$  (LSGO) (100) substrate consists of the {101} planes by observing cross-sectional transmission electron microscopy images of the interface between the PBCO film and the substrate. The images and selected area diffraction patterns show that a mixed c- and b-axis oriented PBCO layer was initially grown on the substrate, followed by pure b-axis oriented PBCO growth. We explain that the c-axis oriented growth is the result of the growth of the PBCO (019) planes on the LSGO (101) planes. We conclude that the nucleation and growth of the PBCO films at the initial stages depends on the crystallographic plane of the substrate surfaces, however, as the film grows further, the kinetics of the deposition process favors b-axis oriented growth.

## I. INTRODUCTION

High-quality a-axis oriented  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (a-YBCO) thin films are very important for making sandwich-type Josephson junctions because of their longer coherence length along the a- or b-axis. The a-YBCO films have been grown by lowering the deposition temperature [1]-[3] or increasing the oxygen pressure [4] as well as using a  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$  (PBCO) or YBCO template on  $\text{SrTiO}_3$  (STO) substrates [5]-[7]. These a-YBCO films have been found to have a low zero resistance temperature ( $T_{c,zero}$ ) of about 80 K because of an oxygen disordering due to the lattice misfit and thermal expansion coefficient mismatch between the cubic STO and non-cubic YBCO films [8], [9]. It has been reported by several groups that an in-plane aligned a-YBCO film having a  $T_{c,zero}$  of 90 K can be realized on tetragonal  $\text{LaSrGaO}_4$  (LSGO) (100) substrates by inserting the YBCO or PBCO template layer between the substrate and a-YBCO films by two step pulsed laser deposition (PLD) [10]-[13].

Cross sectional transmission electron microscopy (TEM) observations of the in-plane aligned a-YBCO films grown on LSGO (100) substrates deposited by a YBCO self-template method were reported by two groups [14], [15]. Miyazawa *et al.* [14] observed a pure a-YBCO growth at the LSGO (100) substrate surface. They proposed a simple growth model of the in-plane aligned a-YBCO thin films on LSGO (100) substrates. The model is based on the atomic-scale geometry of the (100) surface of  $\text{K}_2\text{NiF}_4$ -type substrates, which is charac-

terized by atomic-scale grooves made of oxygen octahedra running along the  $\langle 010 \rangle$  direction. These grooves are assumed to act as preferential nucleation sites of c-axis in-plane aligned a-YBCO. In addition, Mahajan *et al.* [15] reported the cross-sectional TEM image showing a mixed a- and c-YBCO growth at the LSGO (100) substrate surface. They explained that the c-YBCO growth is the result of cation disorder where barium and yttrium ions interchange their respective position in the unit cell during the a-axis growth.

Recently we have reported the superconducting and structural properties of the in-plane aligned a-YBCO films on LSGO (100) substrates fabricated by a PBCO template PLD method, which have a  $T_{c,zero}$  of 88 K and an anisotropy ratio of resistivity of 11.5 at 275 K [13]. However, cross sectional TEM observations of these films have not been reported yet. In this study we report the cross sectional TEM images of the PBCO template films on LSGO (100) substrates and atomic force microscopy (AFM) images of the substrate surface. From our crystallographic orientation analysis for the interface between the PBCO films and the LSGO substrate surface, we will present an understanding of the nucleation and growth of b-PBCO thin films on the substrate surface.

## II. EXPERIMENTAL PROCEDURE

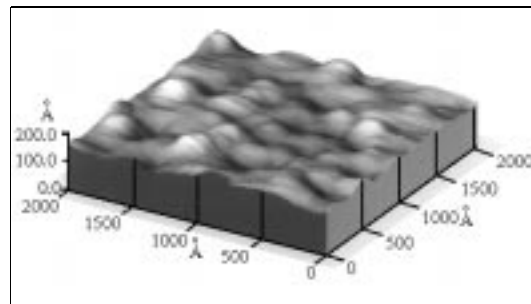
100 nm-thick PBCO films were deposited at 630 °C under an oxygen pressure of 100 mTorr by XeCl excimer laser pulses with an

energy density of  $1 \text{ J/cm}^2$  and a pulse repetition rate of 1 Hz. Subsequent YBCO deposition and annealing processes have been described in detail elsewhere [13]. Hot-pressed stoichiometric YBCO and PBCO targets were mounted on a rotating, water-cooled 4-pole target holder. Mechanically polished LSGO (100) substrates were glued onto the heating block. The substrates, held 4 cm from the targets, were annealed *in situ* at  $850 \text{ }^\circ\text{C}$  for 30 min. under a low base pressure of  $< 10^{-6}$  Torr before the PBCO template deposition in order to remove the impurities and stresses induced from the mechanical polishing. Heating block temperatures measured by a thermocouple inserted into the heating block center were used as the deposition temperature, which were  $20 \sim 90 \text{ }^\circ\text{C}$  higher than that measured by an optical pyro- meter.

Cross-sectional TEM specimens which allowed examination of the interface between the films and the substrate, were prepared in the usual manner. During ion milling, the specimen stage was cooled to 77 K in order to minimize any damage to the film from the ion beam. Images and the selected area diffraction (SAD) patterns were recorded using a CM20T/STEM microscope operated at 200 kV. AFM observations were performed in air at room temperature with a Park Scientific Instrument Auto Probe LS equipped with a small area ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) scanner. Images were obtained in the contact mode using a  $\text{Si}_3\text{N}_4$  AFM cantilever with a large aspect ratio tip.

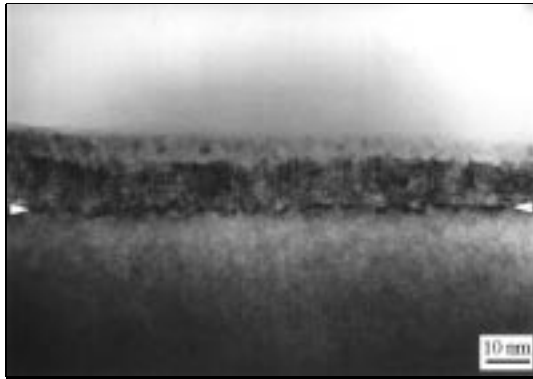
### III. RESULTS AND DISCUSSION

Fig. 1 shows an AFM image of the annealed LSGO (100) substrate surface. A wavy surface was clearly observed. The surface morphology was analyzed as having a root mean square (rms) roughness of 1.4 nm, a mean height of 4 nm, and a peak-to-valley height of 5 nm. It seems that the wavy surface was transformed from a scratched surface of the polished substrate during annealing under high vacuum. Cross sectional TEM image of the interface between the PBCO films and the LSGO (100) substrates is shown in Fig. 2. The wavy interface was also observed in the cross-sectional TEM image. The peak-to-valley height measured from this TEM image was about 5 nm, which is equal to the value obtained from the AFM image.

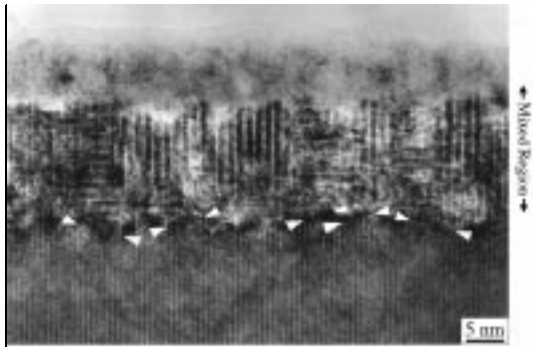


**Fig. 1.** AFM image of the LSGO (100) substrate surface after mechanically polishing and annealing at  $850 \text{ }^\circ\text{C}$  for 30 min.

High-resolution transmission electron microscopy (HRTEM) image of the film-substrate interface is shown in Fig. 3. It is seen from the figure that close to the substrate,

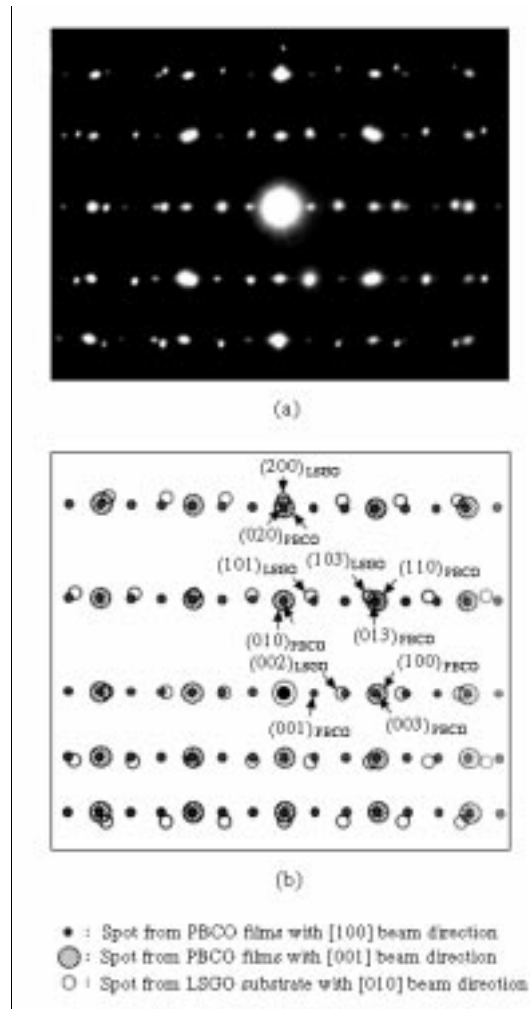


**Fig. 2.** TEM image of the interface between the b-PBCO film and LSGO (100) substrate. This image shows a wavy interface.



**Fig. 3.** HRTEM image of the interface between the b-PBCO film and LSGO (100) substrate. White arrow tips indicate the LSGO {101} planes.

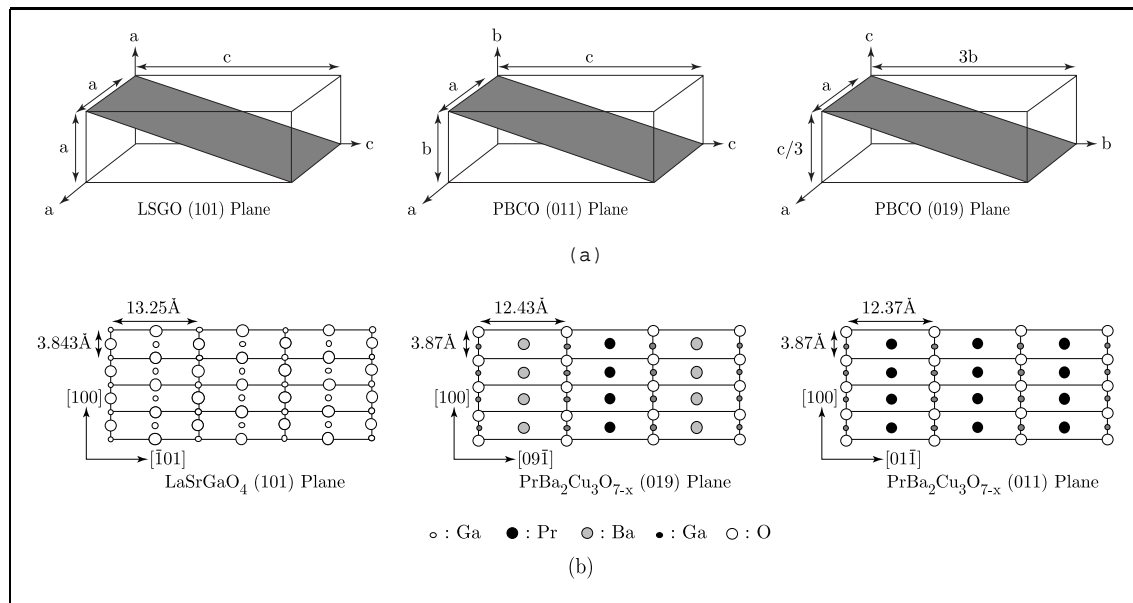
the film has a mixed b- and c-axis orientation followed by pure b-axis oriented growth. We have already reported that the PBCO films have a b-axis orientation [13]. Their orientation relationship has been clearly understood by the lattice matching between the PBCO and the LSGO. SAD patterns and their schematics recorded from the interface shown in Fig. 4 indicate that there is no second phase in the



**Fig. 4.** SAD patterns and their schematics recorded from the interface shown in Fig. 3.

PBCO layer on the LSGO substrate surface.

Inclined planes on the LSGO (100) surface were determined to be the {101} planes by measuring the angle on the HRTEM image in Fig. 3. Considering schematics of the unit cell of PBCO and LSGO as shown in Fig. 5(a), there are two possible PBCO planes, (019)



**Fig. 5.** Schematics of (a) 3-D, and (b) 2-D projections for the LSGO (101), PBCO (019), and PBCO (011) planes.

and (011) planes, which are matched with the LSGO (101) planes. The atomic arrangement of the LSGO (101), PBCO (019), and PBCO (011) planes are described in Fig. 5(b). It is clear from comparing the atomic arrangement of the both PBCO planes that the nucleation and growth of the PBCO (019) plane is more favorable, on the LSGO (101) plane, than the PBCO (011) plane at low temperature, because the nucleation of the PBCO (019) plane is possible without surface diffusion. The (019) plane having a Pr-2Ba arrangement can be easily nucleated after adatom impingement at low temperature. However, the (011) plane having all Pr or all Ba arrangement could be nucleated under high adatom mobility condition, which can be obtained by high substrate temperature or low oxygen pressure or slow

deposition rate. These conditions have been well understood in the a-YBCO and c-YBCO growth mode [16]-[18]. Streiffer *et al.* [16] suggested that the nucleation of a-YBCO domains on the STO (100) substrate is caused by the condition of interface chemistry, surface supersaturation, limited surface diffusion, and Y/Ba disorder or thermodynamic instability. As shown in Fig. 5(a), the c- and b-PBCO domains are clearly the result of the nucleation and growth of the PBCO (019) and (011) planes on the LSGO (101) planes, respectively. Therefore the initial c-axis growth may be due to the preferential growth of the PBCO (019) planes on the LSGO (101) planes. The initial mixed c- and a-axis oriented growth has been observed in the a-YBCO self-template [15]. Cross-sectional TEM image of the a-YBCO

self-template films on LSGO (100) substrate (Fig. 4 in Refs. 15) showed a wavy surface of the substrate.

Further growth of the PBCO films became pure b-axis orientation, after full covering of the wavy LSGO surfaces with the 10 nm-thick mixed b- and c-PBCO layer. It is thus clear that the film orientation in the initial stages strongly depends on the crystallographic planes of the substrate surface at low temperature.

#### IV. CONCLUSIONS

In summary, we have reported the cross-sectional TEM observations of the b-PBCO template layer under the in-plane aligned a-YBCO thin films grown on LSGO (100) substrates by a PBCO template PLD method. Surface morphology of the substrate was wavy in AFM images, this surface consisted of the {101} planes. The mixed c- and b-axis oriented PBCO layer was initially grown on the substrate, followed by pure b-PBCO growth. We analyzed that at the initial stages, the epitaxial growth of the PBCO (019) planes on the LSGO (101) planes provided the formation of the c-PBCO domains. In conclusion, the nucleation and growth of the PBCO films at the initial stages depends on the crystallographic plane of the substrate surfaces at low temperature, as the film grows further, the kinetics of the deposition process favors b-axis oriented growth. In addition, we learned that the preparation of substrate surfaces was criti-

cal to control the initial stage of the film growth and should provide allow for more reproducible deposition conditions and more control over film synthesis. Understanding of the nucleation of high temperature superconducting (HTS) materials on the substrate surface as the film grows, should lead to even better control over the growth process in the near future, and hopefully open the path for the HTS-based electronics to consumer markets.

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