Scanning electron microscopy and resistive transition of \textit{in-situ} grown YBCO films by pulsed laser deposition

M. Branescu, I. Ward, J. Huh, Y. Matsushita, and G. Zeltzer

\textsuperscript{a} National Institute for R\&D Physics of Materials, P.O. Box MG-7, Bucharest, Romania  
\textsuperscript{b} EAG, Sunnyvale, CA 94086, USA  
\textsuperscript{c} Stanford University, Stanford, CA 94305, USA

\section*{Abstract}

In this paper we summarize the deposition parameters, the crystalline structure and the critical temperature of the \textit{in-situ} grown YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} (YBCO) films obtained by pulsed laser deposition (PLD) using our kinetic cool-down regime, described in previous papers. We analyze the resistive transition curves and the corresponding scanning electron microscopy (SEM) pictures of the best \textit{in-situ} grown YBCO films, in order to better characterize the films and refine the deposition process. SEM pictures reveal the typical surface morphology of both \textit{in-situ} grown and post-deposition, oxygen atmosphere annealed YBCO films. A significant smoother surface of the \textit{in-situ} grown films is obtained.

\textbf{Keywords:} YBCO films; \textit{In-situ} PLD growth; SEM

\section*{Introduction}

Fabrication of the \textit{in-situ} grown YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} (YBCO) films by pulsed laser deposition (PLD) produces epitaxial layers upon LaAlO\textsubscript{3} (LAO) substrates, good superconducting properties if the films’ oxygen content is correct and smoother surfaces than those of the post-deposition annealed films. The various experimental parameters of the deposition process affect the microstructure and the quality of the films. For example, by lowering the substrate temperature under 800°C during PLD, or by increasing the thickness of the films over several hundred nanometers, we can alter the amount of \textit{c}-axis oriented crystals, transforming them into \textit{a}-axis oriented crystals in the film. For thicknesses greater than 50 nm the strain already present in the film’s layers close to the substrate lead to a gradual decrease of the film’s surface quality (increased roughness) for thicker films [1,2].

Although the \textit{a}-axis oriented YBCO thin films present always a lower critical temperature than that of the \textit{c}-axis oriented films (about 10 K lower), the study of the \textit{a}-axis oriented films are useful for sandwich-type Josephson junction applications, since the 3 nm coherence length along the \textit{a}-axis is much longer than the 0.7 nm along the \textit{c}-axis one. Therefore, the measurement of the YBCO films surface layers down to nano-scale levels is of the critical importance for multi-layer quantum devices applications [3,4].

In previous papers we reported the \textit{in-situ} growth of the YBCO films, both \textit{c}-axis and \textit{a}-axis oriented, on LAO substrates, by PLD. We achieved films with the critical temperature in the range of 87 K - 90.4 K. We used a kinetic cool-down regime (oxygen pressure – substrate
temperature) technically more advantageous than the usual one, allowing the correct oxygen content without a high temperature post-deposition oxygen annealing process [2,5,6]. We also described the effect of the substrate's surface quality on the epitaxy of the grown films, and the effect of the laser fluence on films' surface quality.

In this paper, we summarize the PLD conditions of the in-situ grown YBCO films and the films’ superconducting and crystallographic properties. SEM pictures revealing the typical and accurate aspect of the three dimensional (3-D) surface morphology of thin and thick in-situ grown YBCO films on LAO substrate are shown. The pictures clearly indicate a significantly smoother surface of the in-situ grown YBCO films in comparison to the post-deposition, oxygen atmosphere annealed films.

**Experiments**

The films were deposited using a KrF excimer laser operating at 248 nm and a pulse repetition rate of 2 Hz on LAO substrates. The distance between the target and the substrate was about 3.5 cm. The laser fluence varied between 2.7 J/cm$^2$ and 4.4 J/cm$^2$ (see Table I). The cool-down kinetic regimes for the best in-situ grown YBCO films by PLD, the substrate temperature, and the oxygen pressure versus time, were detailed in Ref. [2,5,6].

The post-annealing process was done on two samples cut from the #1 and #3 samples of Table 1. Therefore their characteristics (substrate quality and thickness, film thickness) are identical to the above mentioned in-situ films. During the post-annealing process the samples were subjected to oxygen flow at the atmospheric pressure and were also subjected to a thermal process. They were heated from 25 $^\circ$C to 800 $^\circ$C, maintained at this temperature for 2 hours, and then cooled down at a slow rate of 4 $^\circ$C/minute until reaching the final temperature of 25 $^\circ$C. The better characteristics of annealed films were $\delta \sim 0.1$ and, correspondingly, $T_c = 91$ K [7].

We have analyzed the morphological features by SEM, the crystallographic microstructure by X-ray diffraction pattern (XRD), and the superconducting properties of the films by resistive transition measurements. Ref. 2,5,6 detail the results obtained by the XRD techniques. The SEM pictures of the films were obtained with a JEOL type 890 instrument (Figs. 2 and 4) and a Hitachi type S 4700 SEM system (Figs. 3 and 5).

The resistive transitions were measured by the four-point method using a Quantum Design Physical Property Measurement System.

**Results**

The laser parameters (laser fluence and number of laser pulses), the lattice parameters ($c$ lattice constant, “$b-a$” orthorhombic strain, rocking curves’ FWHM, $\delta$ oxygen coefficient) and the critical temperature ($T_c$) are summarized in Table I for the best four PLD runs. The oxygen coefficient $\delta$ in Table I was determined by X-ray diffraction pattern [7].
We consider the run #4 as having the optimized kinetic PLD regime [5], and two YBCO films were in-situ grown during that run, #4A (the best one) and #4B, by using two substrates with very good, but slightly different surface quality.

Some of the defects on the films’ surfaces can be attributed to the large fluctuations of the laser plasma visually noticed during the last PLD runs. The fluctuations are caused by the deterioration of the bulk YBCO target surface by previous PLD processes. A visible gradual deterioration of the target’ surface was developing during the previous depositions, leading us to conclude that a better quality of our in-situ grown films is still possible to obtain. Future work must be done by using a compact high density target with smooth surface in order to improve the uniformity of the YBCO films’ epitaxy and their surface quality.

Figure 1 illustrates the films’ resistance versus temperature (blue, grey, red, green curves), showing the critical temperatures of the samples #1, #2, #3 and #4B from Table I, respectively. All these samples are in pure superconducting orthorhombic phase since the R(T) curves have a sharp transition of the order of 1 K. All R(T) curves present in the normal state good slope intersecting the T axis close to 0 K, indicating that the corresponding films can withstand a high current density. Also, the orientation of their concavity indicates a good oxygenation.

| Sample (film number) | laser fluence (Jcm⁻²) | number of laser pulses (nm) | film thickness (nm) | lattice constant c (nm) | orthorhombic strain b-a (nm) | rocking curves’ FWHM (°) | δ | T_c (K) |
|----------------------|------------------------|-----------------------------|---------------------|------------------------|-----------------------------|--------------------------|---|---------|
| #1                   | 2.7                    | 25,000                      | 850                 | 1.169                  | 0.005                       | 1.0                      | 0.13 | 87      |
| #2                   | 4.2                    | 17,000                      | 1,700               | 1.1696                 | 0.0039                      | 1.3                      | 0.22 | 86.3    |
| #3                   | 3.4                    | 8,140                       | 350                 | 1.1688                 | 0.0046                      | 1.0                      | 0.12 | 88.6    |
| #4A                  | 4.4                    | 9,800                       | 800                 | 1.1687                 | 0.0047                      | 0.4                      | 0.11 | 90.4    |
| #4B                  | 4.4                    | 9,800                       | 800                 | 1.1687                 | 0.0047                      | 0.4                      | 0.11 | 89.7    |
Fig. 1. Resistance vs. absolute temperature T curves: blue, grey, red, green corresponding to the samples #1, #2, #3 and #4B of Table I, respectively. Note that the steps in R(T) curves represent an artifact when the scales of the measurement system are changed near the transition temperatures.

Fig. 2 illustrates the SEM image of the surface of the film #3 of Table I. A good film homogeneity and epitaxy can be inferred from this picture.

Fig. 2. Surface morphology of the in-situ grown YBCO thin film #3 of Table I.
Fig. 3. Typical surface morphology of the in-situ grown YBCO thick film #2 of Table I.

Fig. 4. Typical damaged surface of thin YBCO film #3 of Table I, post-deposition annealed in oxygen atmosphere.
Fig. 5. Typical damaged surface of thick YBCO film #1 of Table I, post-deposition annealed in oxygen atmosphere.

Fig. 3 illustrates the specific surface morphology of the thick film #2. It contains typical features for thick films as flower-like shapes made of particulates rich in BaCuO$_3$, Ba and Cu oxides [8]. Three different magnifications of the SEM pictures are displayed in the figure.

Figs. 4 and 5 present the specific damaged surfaces of a thin and a thick YBCO film post-deposition annealed in the oxygen atmosphere, listed in Table I with #3 and #1, respectively. We notice that the post-deposition annealing process in the oxygen atmosphere dramatically worsens the films’ surface.

**Conclusion and future works**

In this paper we summarize our best four PLD runs to obtain in-situ grown YBCO films detailed in previous papers [2,5,6]. Typical SEM pictures of thin and thick in-situ deposited YBCO films on LAO substrate, and also of post-deposition oxygen annealed YBCO films are shown. These pictures demonstrate the advantage of in-situ growing YBCO films by PLD, the technique providing much smoother film’s surface than that of the post-deposition annealed films. As a powerful and useful tool, SEM illustrates the accurate pictures of the films’ surface morphology with high resolution. During the optimized PLD run, achieving a c-axis oriented film with 90.4 K critical temperature, large laser plasma fluctuations were observed. For the future work, to further improve the YBCO films quality, we consider to use a compact target with better surface,
to lower the laser fluence, to correspondingly adjust the total number of the laser’ pulses for a certain film thickness, to refine the pulse repetition rate of the laser and the distance target-substrate in the PLD process.

Acknowledgments

The first author is grateful to Prof. M. Beasley, Prof. R. Hammond, Prof. I. Fisher, and Prof. H. Manoharan, GLAM, Stanford University, for fruitful discussions and help to obtain accurate measurements at cryogenic temperatures.

References

[1] D. B. Chrisey, G. K. Hubler, Pulsed Laser Deposition of Thin Films, John Wiley & Sons Inc., NY, 1994 (Chapters 5, 14, 15).
[2] M. Branescu, A. Vailionis, I. Ward, J. Huh, and G. Socol, “In situ grown epitaxial YBa$_2$Cu$_3$O$_{7-x}$ thin films by pulsed laser deposition under reduced oxygen pressure during cool-down time”, Appl. Surf. Sci. 252, 4573 (2006).
[3] E. Dieckmann, R. Kursten, M. Lohndorf, and A. Bock, “Epitaxial quality of c-axis and a-axis oriented of YBa$_2$Cu$_3$O$_7$ films. Characterisation by Raman spectroscopy”, Physica C, 245, 212 (1995).
[4] Gun Yong Sung, Jeong Dae Suh, and Sahn Nahm, “Epitaxial relationships of the a-axis oriented YBa$_2$Cu$_3$O$_{7-x}$ thin films on PrBa$_2$Cu$_3$O$_{7-x}$ buffered SrTiO$_3$ (100) by two step PLD”, in MRS Symposium Proceedings, Vol. 341, 177 (1994).
[5] M. Branescu, A. Vailionis, G. Socol, and A. Moldovan, "AFM and complementary XRD measurements of in-situ grown of YBCO films obtained by pulsed laser deposition", Appl. Surf. Sci. 253, 8179 (2007).
[6] M. Branescu, V. S. Teodorescu, G. Socol, I. Balasz, C. Ducu, and J. Jaklovszky, "Experiments on pulsed laser deposition and characterization of epitaxially in-situ grown YBa$_2$Cu$_3$O$_{7-x}$ thin films", J. Optoel. Adv. Mat. 7, 967 (2005).
[7] K. Conder, D. Zech, Ch. Kruger, E. Kaldis, H. Keller, A. W. Hewat, and E. Jilek, “Indication for a Phase Separation in YBa$_2$Cu$_3$O$_{7-x}$ “ in: Phase Separation in Cuprate Superconductors, E. Sigmund, K. A. Muller (Eds.), Springer, Berlin, 1993, pp. 210.
[8] S. Proyer, E. Stangl, M. Borz, B. Hellebrand, and D. Bäuerle, "Particulates on pulsed laser deposited Y-Ba-Cu-O films", Physica C 257, 1 (1996).