Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica C 405 (2004) 127–132
PHYSICA C
www.elsevier.com/locate/physc

HRTEM characterization of $YBa_2Cu_3O_{7-\delta}$ thick films on $LaAlO_3$ substrates

Jianming Zeng [a,*], Jie Lian [b], Luming Wang [b], Penchu Chou [a], Alex Ignatiev [a]

[a] *Texas Center for Superconductivity and Advanced Materials, University of Houston, Houston, TX 77204-5002, USA*
[b] *Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109-2104, USA*

Received 10 September 2003; received in revised form 30 January 2004; accepted 10 February 2004
Available online 5 March 2004

Abstract

High-quality superconducting $YBa_2Cu_3O_{7-\delta}$ (YBCO) thick films with thickness over 2 μm were grown on $LaAlO_3$ (LAO) substrates by photo-assisted metalorganic chemical vapor deposition (PhA-MOCVD) with a single liquid precursor delivery system. The YBCO thick films fabricated are single-crystal like with no visible grain boundaries or voids. Surface and interface microstructures of YBCO thick films have been systematically investigated by scanning electron microscopy, high-resolution transmission electron microscopy, and selected area electron diffraction. Large precipitates were observed on the surface of these films. These precipitates are mostly composed of crystalline $BaCu_3O_4$, along with some polycrystalline and amorphous YBCO phases, and were found to exist only on top of the YBCO films, with no penetration into the films. The high quality of the prepared YBCO thick films was confirmed further by the results of X-ray diffraction and T_c/J_c measurements. Thus, these thick YBCO films prepared by PhA-MOCVD have promising application potential in fields such as coated conductors.

1. Introduction

For crystalline advanced materials, such as the high temperature oxide superconductors, the preparation of defect-free thin/thick films is highly desired as it opens the doors to fundamental studies and the development of the attractive commercial applications, such as in the fields of microelectronics and high current devices [1,2]. High temperature superconducting thin/thick films, especially $YBa_2Cu_3O_{7-\delta}$ (YBCO), deposited on various substrates have been attracted much attention in recent years because of their unique properties of high film quality, high critical temperature (T_c), high critical current density (J_c) and low microwave surface resistance (R_s). Numerous investigations on microstructures of YBCO thin films (thickness $\leqslant$ 1.0 μm) prepared by various deposition techniques have been extensively performed [3–9]. However, to our knowledge, no attempts have been made to systematically investigate the microstructures of YBCO thick films (thickness > 1.0 μm). For this reason, a deeper understanding of microstructures of YBCO thick films, especially the nature of defects on the surface and interface, are needed in order to improve

* Corresponding author. Tel.: +1-713-7438233; fax: +1-713-7477724.
E-mail address: jmzeng@svec.uh.edu (J. Zeng).

0921-4534/$ - see front matter
doi:10.1016/j.physc.2004.02.002

the epitaxial properties and crystalline quality of YBCO thick films for the practical applications to devices, such as second-generation coated conductors.

In this paper, we present a high-resolution transmission electron microscopy study of the atomic structure of YBCO thick films and the interface between the YBCO films and the LAO substrates. In particular, a new type of crystalline phase, $BaCu_3O_4$, was found on the surfaces of these YBCO thick films.

2. Experimental

High quality YBCO thick films were grown on LAO (0 0 1) substrates by photo-assisted metalorganic chemical vapor deposition (PhA-MOCVD) with a single liquid precursor delivery system. The metalorganic precursors of the type $Me(TMHD)_n$ (Me = Y, Ba, Cu; TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate) were dissolved in mixtures of tetrahydrofuran (THF), isopropanol (IPA) and tetraglyme. This solution was delivered into a preheated evaporator where then the precursor/solvent solutions were vaporized in the flash evaporator and transported by a carrier gas into the vertical quartz reactor. Energy for the reaction was supplied solely by tungsten halogen (TH) lamps. The detailed deposition parameters were reported elsewhere previously [10]. YBCO thick films with thickness of 2–4 μm were reproducibly grown on LAO substrates at a deposition temperature of ~800 °C by this photo-assisted MOCVD technique at a high growth rate of 0.1–0.5 μm/min.

The YBCO thick films deposited on LAO substrates were routinely examined by X-ray diffraction (XRD) and T_c/J_c measurements to insure their high crystalline and superconducting properties. XRD θ–2θ scans (for phase development), ω-scans (for out-of-plane texture) and ϕ-scans (for in-plane texture) were performed in a Philips D5000 and a Siemens GADDS system. T_c/J_c of the YBCO thick films was obtained by standard four-point-probe resistivity measurements with zero applied field.

Cross-sectional samples were made by mechanical polishing, followed by a 4 KeV Ar^+ ion milling to obtain a thin area suitable for transmission electron microscopy observation. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were then performed on the thick films by using a JEOL 2010F transmission electron microscope operating at an accelerating voltage of 200 kV. The surface morphology and cross-sectional image of the prepared YBCO thick films was also investigated by a JEOL JSM5401 scanning electron microscopy (SEM).

3. Results and discussion

3.1. XRD, T_c/J_c, and SEM analyses

The thick YBCO films presented here are strongly textured both in-plane and out-of plane. The high crystalline quality of a typical YBCO film (2.2 μm thick) can be seen in the XRD data of Fig. 1. The θ–2θ scan (Fig. 1(a)) reveals that the film is fully c-axis oriented. The out-of-plane crystallographic texture is determined from the XRD rocking curve (ω-scan), which for the (005) peak shows a FWHM of only 0.21°. The in-plane

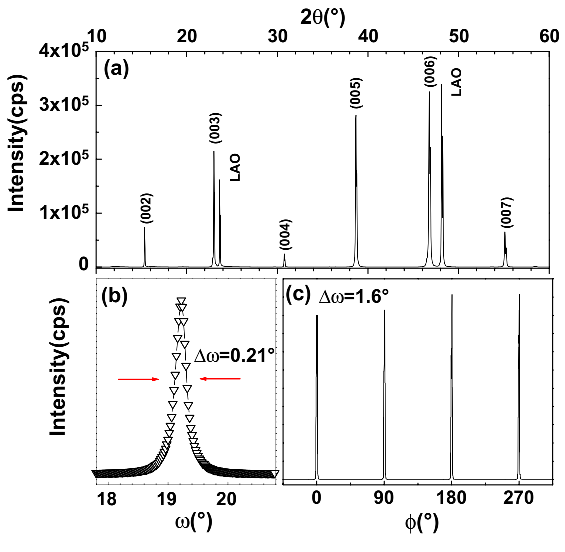

Fig. 1. X-ray diffraction data for a 2.2 μm-thick YBCO film deposited on a LAO (0 0 1) substrate by the photo-assisted MOCVD technique: (a) θ–2θ scan, (b) ω-scan for the YBCO (0 0 5) reflection, and (c) ϕ-scan for the YBCO (1 0 3) reflection.

crystallographic alignment of this thick YBCO film as determined by the XRD ϕ-scan through the (1 0 3) peak (Fig. 1(c)) shows a FWHM of ~1.6°. This data clearly indicates that the YBCO thick film obtained by the PhA-MOCVD technique possess high crystalline quality.

The superconducting transition temperature (T_c) and critical current density (J_c) data are shown in Fig. 2(a) and (b). The T_c value was found to be ~90.0 K with a transition width (ΔT_c) of less than 1.0 K. The insert, Fig. 2(b) shows the voltage-current density (V–J) characteristic at 77 K. We find a self-field critical current density (J_c) of $\sim 1.3\times 10^6$ A/cm^2 at 77 K using the voltage criterion of 1 μV/cm.

Fig. 3 shows the scanning electron microscopy (SEM) image for the 2.2 μm thick film. Some precipitates were found to populate the surface of the YBCO. Such particles or precipitates along with surface voids have been typically seen on the YBCO thick films obtained by conventional MOCVD techniques [12,13]. However Fig. 3 reveals that the present YBCO thick films prepared by PhA-MOCVD have very dense and pinhole-free surface morphology. The cross-sectional SEM image of this YBCO thick film (Fig. 4) further indicates a dense, pinhole-free and void free film structure, with minimal grain boundaries observed

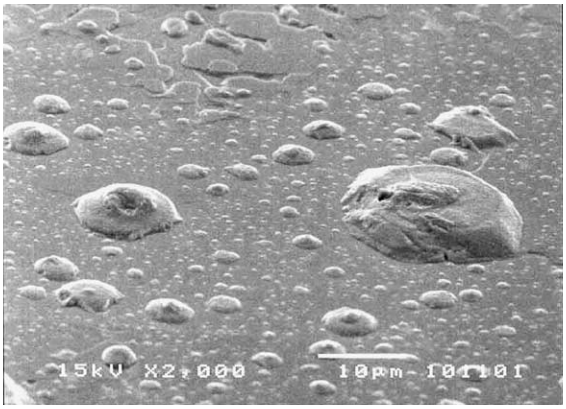

Fig. 3. A typical SEM micrograph of the surface of a YBCO thick film deposited on an LAO substrate by the photo-assisted MOCVD method.

in the film matrix. It has been previously shown that a void-rich layer is generally found at or near the surface of thick YBCO films (thickness > 1 μm) deposited by techniques other than PhA-MOCVD, such as pulsed laser deposition (PLD) or conventional MOCVD [12–15]. This void layer exhibits degraded crystal structure, and results in a reduction of critical current density (J_c). A possible

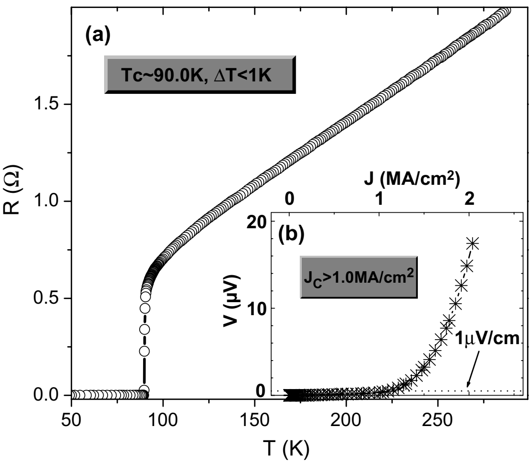

Fig. 2. (a) Temperature dependence of resistance, and (b) voltage vs. current density curve at 77 K and zero field for a 2.2 μm-thick YBCO film.

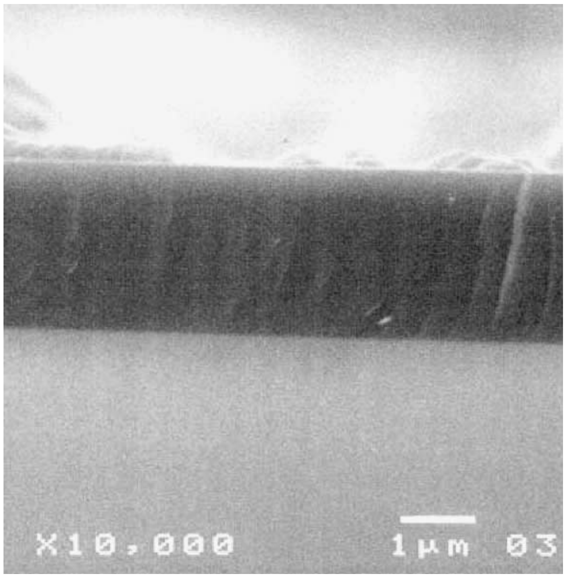

Fig. 4. A cross-sectional SEM micrograph of a 2.2 μm thick YBCO film deposited on an LAO substrate.

reason for such void formation with respect to film growth technique has been reported elsewhere [11]. However, as shown in Figs. 3 and 4, the YBCO thick film presented here can maintain a void-free film structure for film thickness > 1 μm, which is very important for practical applications of YBCO thick films.

3.2. HRTEM and SAED analyses

High resolution TEM (HRTEM) and selected area electron diffraction (SAED) studies were undertaken in order to characterize the precipitates on film surface and to study the interface region between the YBCO layer and its LAO substrate. As shown in Fig. 5, a total of four areas of the YBCO film were selected for this study: area *A* is the interface between the YBCO thick film and its LAO substrate; area *B* is the bulk of the YBCO film matrix; area *C* is the interface between the YBCO film and a large precipitate on top of the film; and area *D* is the bulk of the large precipitate.

Fig. 6 shows the HRTEM image and SAED pattern of the interface between the YBCO thick film and the LAO substrate (area *A* of Fig. 5). In this HRTEM image, the thick film is atomically ordered, and its atomic arrangement is coherent with the lattice of the LAO (1 0 0) substrate. This indicates that the YBCO thick film has grown epitaxially on the LAO substrate by the PhA-MOCVD technique. It is also seen in Fig. 6 that in the interface region there are no traces of imperfections, such as voids or disorder, which are often

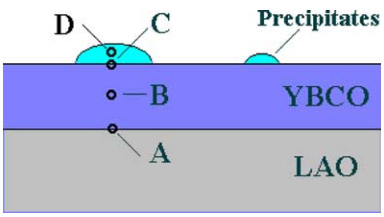

Fig. 5. The schematic diagram of the cross-section of a YBCO thick film identifying the four different regions where HRTEM measurements were performed: (A) the interface between the YBCO film and the LAO substrate; (B) the YBCO thick film matrix; (C) the interface between the YBCO film and a large precipitate on the surface of the YBCO thick film; and (D) the bulk of a precipitate on the YBCO film surface.

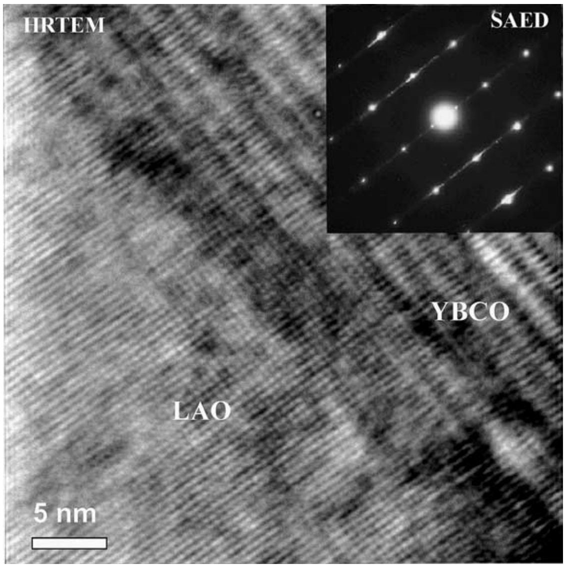

Fig. 6. HRTEM image and SAED pattern of the interface area between the 2.2 μm thick *c*-axis-oriented YBCO film and the LAO substrate (area *A* of Fig. 5), showing atomically aligned epitaxial growth of the YBCO thick film on the LAO substrate.

found in YBCO thick films grown by techniques other than PhA-MOCVD [16,17]. The HRTEM and SAED patterns of area *B* (bulk matrix of the thick YBCO film) are shown in Fig. 7, and indicate that the YBCO film is of high crystalline quality, and free of other phase. The microstructural analyses of the interface and bulk of the YBCO thick film are consistent with the XRD analyses presented in last section, indicating further that the YBCO thick film is of high crystalline and epitaxial quality.

Fig. 8 shows the HRTEM image and SAED data from a precipitate on top of the YBCO film (area *D*). The data indicate the presence of crystallites in the precipitate which show an orthorhombic structure with space group of C_{mmm}, along with lattice parameters of $a = 1.098$ nm, $b = 0.55$ nm, and $c = 0.392$ nm, can be assigned to these crystallites. These crystallographic results are consistent with that of $BaCu_3O_4$ as reported by Bertinotti et al. [18]. Chemical composition of the crystallites has been previously defined by EDS analysis [11].

The HRTEM image of the interface area between the YBCO film and the precipitate (area *C*)

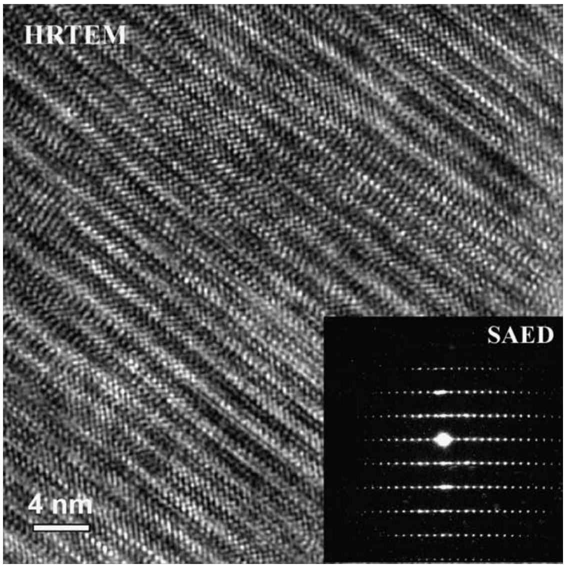

Fig. 7. HRTEM image and SAED pattern of the matrix of the 2.2 μm thick YBCO film (area *B* of Fig. 5).

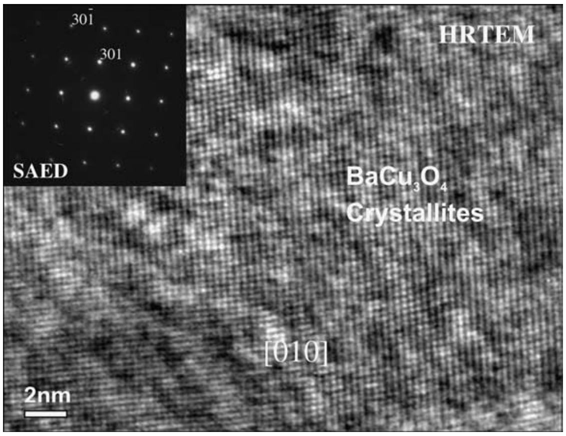

Fig. 8. HRTEM image and SAED pattern of the bulk of the precipitate (area *D* of Fig. 5) showing $BaCu_3O_4$ crystallites.

is shown in Fig. 9. Here the $BaCu_3O_4$ phase is poorly ordered, showing essentially no crystalline structure at the interface. However, polycrystalline YBCO grains and amorphous YBCO layers can be observed in this interface region. There are no signs of CuO or Y_2O_3 in this region, though impurity phases such as these have been usually found at the surface of YBCO films [19]. It should be noted that the appearance and size of the pre-

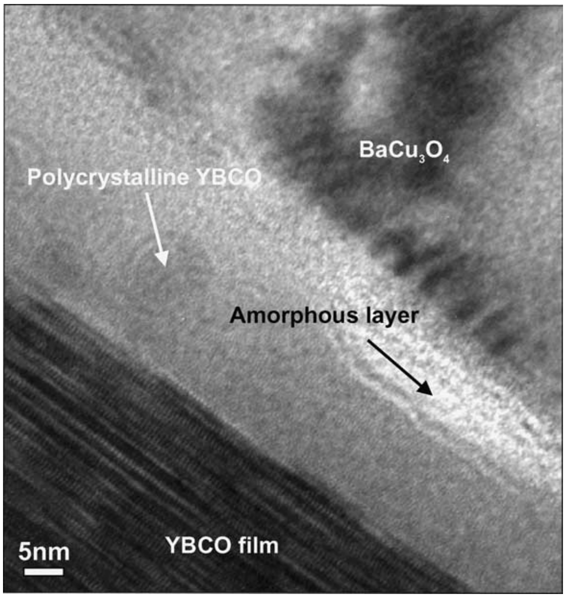

Fig. 9. HRTEM image of the interface between the YBCO thick film and a large precipitate on the film surface, (area *C* of Fig. 5), indicating the presence of polycrystalline and amorphous YBCO phases and amorphous $BaCu_3O_4$ in this region.

cipitates on the surface of YBCO films grown by PhA-MOCVD do not depend on the on thickness of the YBCO films [10]. The origin of these precipitate phases on top of thick YBCO films grown by PhA-MOCVD is under investigation.

4. Conclusion

High quality YBCO thick films prepared by PhA-MOCVD with a single liquid precursor delivery system have been studied for crystallographic and superconducting quality. It was found that the YBCO thick films were of high crystalline quality with excellent epitaxial orientation to the LAO substrate, with an atomically perfect and sharp interface with the LAO substrate. The bulk of the YBCO films were very dense, with no visible voids, grain boundaries, or secondary phases in film matrix. On the other hand, $BaCu_3O_4$ precipitates were identified on the surface of the YBCO film. Polycrystalline and amorphous YBCO phases were found between the precipitates and the YBCO film matrix, however, thee phases and the precipitates did not penetrate into the YBCO film, thus not impacting the J_c of the films which was measured to be $>1.3 \times 10^6$ A/cm^2 for a 2.2 μm thick YBCO film. Thus, potentially these thick YBCO films made by PhA-MOCVD could be used in coated conductor technology for high current capacity wire.

Acknowledgements

The authors would like to thank Xin Zhang, ZhongJia Tang and Nick Stoffle for their assistance in this work, and give special thanks to Prof. Naijuan Wu, for numerous productive discussions. This work was supported in part by DOE through Lockheed Martin, TcSAM, NASA, the State of Texas through ATP/ARP, and the R.A. Welch Foundation.

References

[1] D.P. Norton, A. Goyal, J.D. Budai, D.K. Christen, D.M. Kroeger, E.D. Specht, Q. He, B. Satfian, M. Paranthaman, C.E. Klabunde, D.F. Lee, B.C. Sales, F.A. List, Science 274 (1996) 755.
[2] Y. Yoshida, I. Hirabayashi, H. Kurosaki, H. Akata, K. Higashiyama, Y. Takai, IEEE Trans. Appl. Supercond. 11 (1) (2001) 3453.
[3] J. Hasen, D. Lederman, I.K. Schulle, Phys. Rev. Lett. 70 (1993) 1731.
[4] Q. Jin, S.W. Chan, J. Mater. Res. 17 (2) (2002) 323.
[5] K. Develos, H. Yamasaki, A. Sawa, Physica C 357 (2001) 1353.
[6] W.C. Goh, S.Y. Xu, S.J. Wang, J. Appl. Phys. 89 (8) (2001) 4497.
[7] C. Dubourdieu, J.P. Senateur, O. Thomas, IEEE Trans. Appl. Supercond. 7 (2) (1997) 1268.
[8] E. Olsson, K. Char, Appl. Phys. Lett. 64 (10) (1994) 1292.
[9] D.P. Norton, D.H. Lowdes, Appl. Phys. Lett. 63 (10) (1993) 1432.
[10] J. Zeng, P. Chou, X. Zhang, Z.J. Tang, A. Ignatiev, Physica C 377 (2002) 235.
[11] J. Zeng, P. Chou, A. Ignatiev, J. Lian, L. Wang, IEEE Trans. Appl. Supercond., in press.
[12] S.R. Foltyn, Q.X. Jia, P.N. Kinder, Y. Fan, J.F. Smith, Appl. Phys. Lett. 75 (1999) 3692.
[13] V. Selvamanickam, G. Carota, M. Funk, N. Vo, P. Haldar, U. Balachandran, M. Chudzik, O. Arendt, J.R. Groves, R. DePaula, B. Newman, IEEE Trans. Appl. Supercond. 11 (1) (2001) 3379.
[14] Y. Yoshida, Y. Ito, H. Nagai, Y. Takai, I. Hirabayashi, S. Tanaka, Physica C 320 (1998) 31.
[15] J.P. Senteur, F. Felten, S. Pignard, F. Weiss, A. Abrutis, V. Bigelyte, A. Teiserskis, Z. Saltyte, B. Vengalis, J. Alloy Compounds 251 (1997) 288.
[16] P.B. Mozhaev, F. Ronnung, P.V. Komissinskii, Physica C 336 (1–2) (2000) 93.
[17] D.G. Andrianov, S.O. Klimonsky, V.B. Beklemishev, Superlatt. Microst. 25 (3) (1999) 533.
[18] A. Bertinotti, J. Hammann, D. Luzet, E. Vincent, Physica C 160 (1989) 227.
[19] J. Santiso, A. Figueras, A. Moya, Physica C 351 (2) (2001) 155.