Journal of Alloys and Compounds 566 (2013) 175–179

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

The effects of the post-annealing temperature on the growth mechanism of $Bi_2Sr_2Ca_1Cu_2O_{8+\partial}$ thin films produced on MgO (1 0 0) single crystal substrates by pulsed laser deposition (PLD)

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ARTICLE INFO

Article history:
Received 8 January 2013
Received in revised form 3 March 2013
Accepted 5 March 2013
Available online 20 March 2013

Keywords:
Bi-2212 thin film
Pulsed laser deposition (PLD)
Post-annealing
Critical current density
Superconductivity
Magnetic hysteresis

ABSTRACT

The effects of post-annealing temperature were investigated on $Bi_2Sr_2Ca_1Cu_2O_{8+\partial}$ thin films deposited on MgO (1 0 0) substrates by pulsed laser deposition (PLD). The structural and superconducting properties of the films have been determined by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature dependent resistivity (*R*–*T*), and DC magnetization measurements. The films which were deposited at 600 °C were post-annealed in an atmosphere of a gas mixture of Ar (93%) and O_2 (7%), at temperature ranging between 800 and 880 °C. This resulted in films which exhibited a single phase of 2212 with a high crystallinity (FWHM $\approx$ 0.16°) and texturing along the *c*-axis, perpendicular to the plane of the substrate. An optimum temperature of 860 °C was found for the post-annealing thermal treatment. The critical temperature, T_C, of the films was measured as 82 K and the critical current density, J_C, was calculated as 3×10^7 A/cm^2 for the film annealed at 860 °C.

1. Introduction

The discovery of high temperature superconductors has opened a new way for their applications in technologically important areas [1]. However, depending on the specific applications, it is necessary to synthesize them in specific forms like thin films [2–24]. Superconducting electronics devices require having high quality thin films, with high T_C values and very smooth surfaces as well as in single crystalline form. In particular, the use of high quality high-T_C thin films is important for device applications like SQUIDs [22,25], THz radiation sources [26], bolometers [23], intrinsic Josephson junctions [17,27], and other cryo-electronic devices.

The BSCCO system was discovered by Michel et al. [28] and subsequent work reported by Maeda et al. [29] for the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ (n = 1,2,3) superconductor family. The BSCCO system is one of the most studied members of the high-T_C family of superconductors. Since Bi-2212 is more stable than Bi-2223, which can only be obtained within a very narrow temperature window [30–32], it is easy to produce Bi-2212 phase in thin film form. The thin films of the Bi-2212 phase can be synthesized with various methods, such as molecular beam epitaxy (MBE) [33,34], DC sputtering [35], RF sputtering [36], chemical vapor deposition (CVD) [37,38], and pulsed laser deposition (PLD) techniques [2,3,9,13].

Pulsed laser deposition (PLD) was first introduced to deposit YBCO films on various substrates [39], and has later found a wide use in obtaining high-T_C thin films with good quality. Many efforts have been put to improve the superconducting properties of Bi-2212 thin films deposited onto single crystal substrates, such as MgO. In early studies [14,16], it was observed that the BSCCO thin films produced by PLD have exhibited poor superconducting properties compared to alternative fabrication techniques. It has been recently reported, for example, that high T_C and J_C values may be obtained for these high-T_C materials produced by continuous laser irradiation methods [40–42]. On the other hand, it was reported that a significant improvement in superconducting properties of the thin films could be obtained, deposited by PLD and applying a post-annealing heat treatment in an atmosphere containing a mixture of argon and oxygen (Ar: 93,O_2: 7) [9,13,15,17]. Among various factors, the quality of the substrate also affects directly the superconducting properties of the thin films.

In this study, we have reported our results on the effects of the post-annealing temperature on the Bi-2212 thin films deposited on MgO (1 0 0) single crystal substrates by pulsed laser deposition.

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http://dx.doi.org/10.1016/j.jallcom.2013.03.054

2. Experimental

The $Bi_2Sr_2Ca_1Cu_2O_{8+\partial}$ target was prepared via conventional solid state reaction. The Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO starting materials were mixed and calcined twice at 750 °C and 800 °C for 24 h. The resulting powders were then pressed into 1 inch diameter pellets by applying 14 tons of pressure and it was sintered twice at 820 °C. Finally, the pellet was annealed at 860 °C for 60 h. After each thermal treatment a milling process also followed.

The thin films of $Bi_2Sr_2Ca_1Cu_2O_{8+\partial}$ were deposited onto MgO (1 0 0) substrates by pulsed laser deposition (PLD), using an excimer laser (248 nm) focused on the target surface at an angle of 45°. Before deposition (at base pressure 1.0×10^{-6} -Torr), substrates were first heated up to 1000 °C at a rate of 30 °C/min, soaked during 15 min to clean remaining impurities from their surfaces, and then cooled down to 600 °C. This, we believe, helps also to relieve any stresses build up on the substrate. During the deposition, the substrates were kept at 600 °C while keeping O_2 gas pressure in the chamber fixed to 250 mTorr. The distance between the substrate and the target was 45 mm. The laser fluence was kept at $\sim$2.39 J/cm^2 and with a pulse repetition rate of 5 Hz. After deposition, the substrates were cooled down to room temperature at a rate 20 °C/min, while maintaining the pressure of O_2 gas at 70 Torr. After deposition, the post-annealing heat treatments were performed in a quartz tube having a mixture of (Ar/O_2: 93/7) inside, and the tube was placed inside of a tubular furnace heated at temperatures in the range 800–880 °C during 10 min.

After the heat treatment process, the crystal structure and phase formation of the films were analyzed by using X-ray diffraction patterns with a Rigaku MiniFlex diffractometer with Cu Kα radiation and a scan rate 1°/min between 2θ = 10–70°. The surface morphology and compositional analyses of thin films were also investigated by SEM and EDX measurements by using field emission SEM of (FEG model QUANTA 250). The surface morphology and roughness were observed by atomic force microscopy (scanning area: 10 × 10 μm^2). The thickness was measured with a profilometer as 500 nm. In order to determine the critical superconducting temperatures, magnetic measurements were also carried out in a model 7304 Lake Shore Vibrating Sample Magnetometer (VSM) system under ZFC mode, under a magnetic field of 50 Oe applied perpendicular to the film surface. In order to determine the zero resistivity critical temperature, we have used a home-made conventional four probe method with a closed cycled liquid He refrigerator and temperature controller. The J_Cs were estimated from the M–H loops as measured in between −0.5 and 0.5 T magnetic field applied perpendicular to the film surface having a rectangular shape.

3. Results and discussion

3.1. XRD characterization

Fig. 1 shows the XRD patterns of the thin films prepared with post-annealing heat treatment between 800 and 880 °C. It is seen that the peak intensity of the films significantly increases with the increasing annealing temperature, and all main peaks were constructed on the (0 0 l) lines of Bi-2212 phase. This indicates a certain degree of texture in the film along the *c*-axis, which is perpendicular to the plane of the MgO (1 0 0) substrate.

Additionally, the film grown at a temperature of 800 °C contains small amounts of the phase Bi-2201, which has a lower superconducting critical temperature. From their comparison, the films annealed at higher temperatures, namely at 860 and 880 °C, show better crystallization properties with higher peak intensities. On the other hand, a very small part of the film material from the surface of the film, grown at 880 °C, has been lost during annealing at high temperature. This may be due to a bad adhesion of the film onto the surface of the MgO substrate. Finally, it is possible to say that after the post-annealing temperature at 820 °C, all visible peaks recorded by using International Center for Diffraction Data (ICDD) catalogue have pointed out the majority of Bi-2212 superconducting phase. The full widths at the half-maximum values (FWHM) of the (0 0 10) peak of the films annealed at 860 and 880 °C were determined as 0.161° and 0.158°, respectively. The lattice parameter *c* and crystal size *L* of the films were calculated from XRD diffraction patterns as given in Ref. [43], and are given in Table 1.

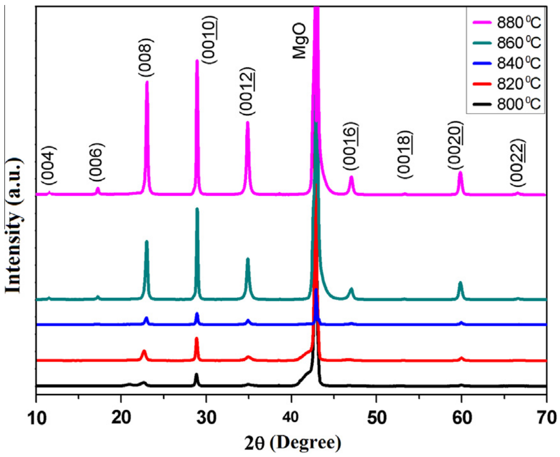

Fig. 1. XRD patterns of films annealed between 800 and 880 °C.

Table 1
Lattice parameter *c* and crystal size *L* versus post-annealing temperature.

Post-annealing temperature	*c* (Å)	Crystal size *L* (Å)
880	30.868	589.64
860	30.870	565.03
840	30.890	461.48
820	30.867	430.45
800	30.910	388.44

3.2. SEM analysis

The SEM photographs of thin films prepared with post-annealing heat treatment at 860 and 880 °C are given in Fig. 2. It can clearly be seen that the main matrices of the films contain well stacked terrace-like grain structures and are layered mainly *c*-axis oriented. Moreover, the voids among the grains on the film surface annealed at 860 °C appear larger compared to the film annealed at 880 °C. The film annealed at 880 °C has larger grains and well oriented terrace-like grain boundaries indicating the existence of the Bi-2212 phase [44].

3.3. AFM analysis

Finally, the surface morphology image observed with AFM on the film annealed at 860 °C is given in Fig. 3. The AFM scanning area was a 10 μm square. The roughness profile under the selected line demonstrates that the heights of the steps oscillate in maximum range of two *c*-axis of the 2212 phase. A localized, well packed grain structure, oriented along the *c*-axis, was observed in the main matrices.

3.4. Magnetic properties

The DC magnetization measurements of all films are given in Fig. 4. The T_Cs of the films annealed at 800, 820, 840, 860, and 880 °C were determined as 42, 75, 76, 82 and 80 K, respectively. It can be observed that all samples display a typical diamagnetic behavior. On the other hand, the diamagnetic signal and the critical temperature, T_C, smoothly decreases and shifts towards lower temperatures with increasing annealing temperature. For the post-annealing temperatures at and above 820 °C, the sharp superconducting transitions are observed around the critical temperature, T_C. These sharp transitions indicate a good quality and homogeneity of the films. The film annealed at 800 °C exhibits mainly the low temperature phase (Bi-2201). The highest critical temperature was obtained for the film annealed at 860 °C. This T_C value is about in accordance with 85 K as measured for the $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ target.

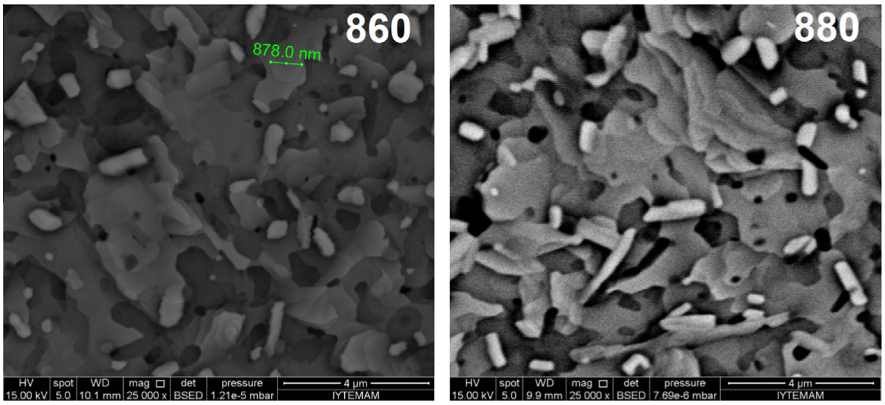

Fig. 2. SEM images of the films annealed at 860, and 880 °C.

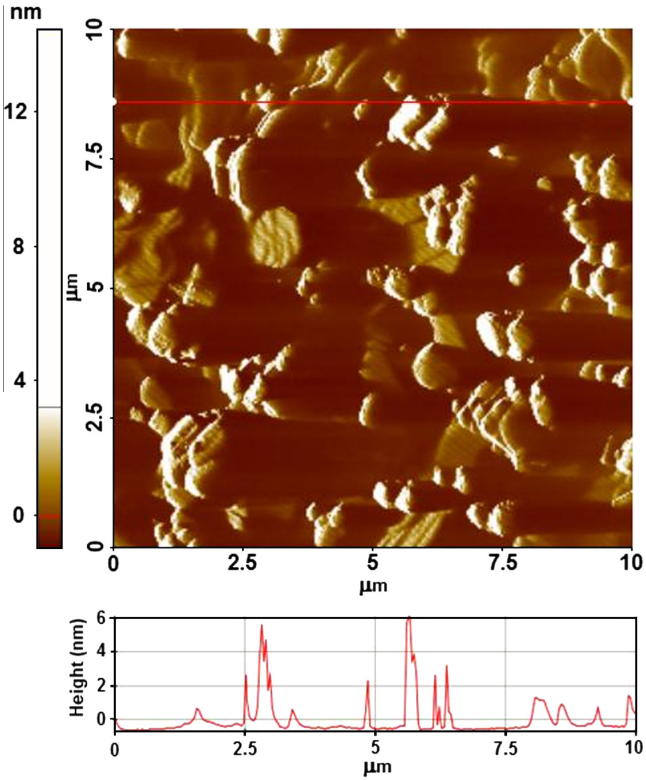

Fig. 3. AFM images of the film annealed at 860 °C.

3.5. Electrical measurement

The temperature dependence of the resistivity of the films annealed at 860 and 880 °C is given in Fig. 5. The resistance arising from copper contacts was determined as 0.40 Ω. By taking into account this value, the zero resistivity transitions T_{C0} of the films were obtained as 89 K and 87 K, and the superconducting transition widths (ΔT) varies as 6 K and 5 K, respectively. It may be stated that both films have almost a single phase with a sharp transition around T_C.

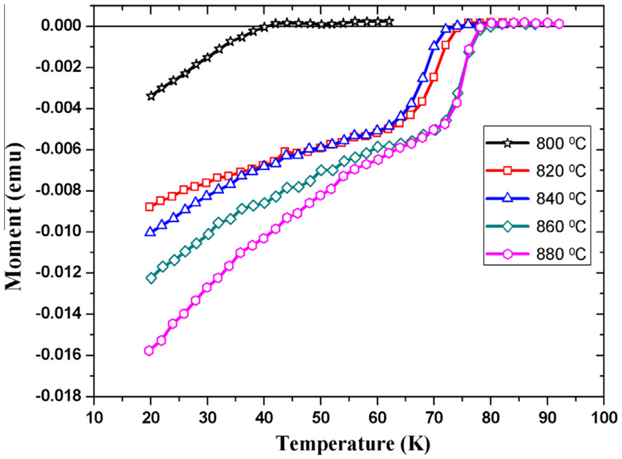

Fig. 4. DC magnetic moments versus temperature in 50 Oe ZFC modes for annealed films at 800–880 °C.

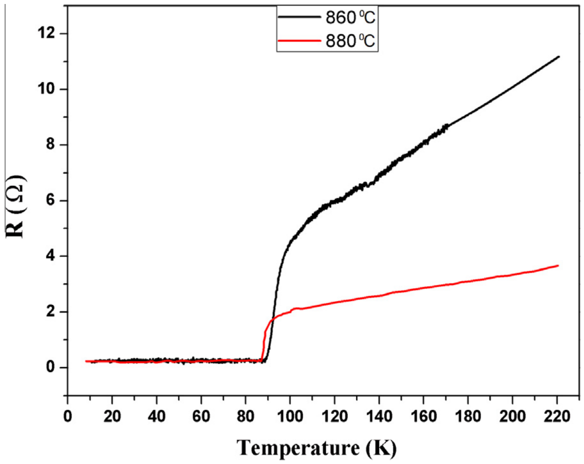

Fig. 5. R–T measurements of the films annealed 860, and 880 °C.

3.6. Magnetic hysteresis

The magnetic hysteresis cycles (M–H) of the films were performed between the fields of ±5 kOe at 10 K, and given in Fig. 6. It is easily seen that, while the annealing temperature increases, the area of hysteresis loops remarkably becomes larger. It is attributed to the fact that an increase of the annealing temperature leads to a stronger grain structure, stemming from a better crystallization process taking place. The film produced at 800 °C demonstrates typical curves of low temperature phase (Bi-2201).

We have calculated the critical current density J_C of the films by using the Bean model as given in [45]:

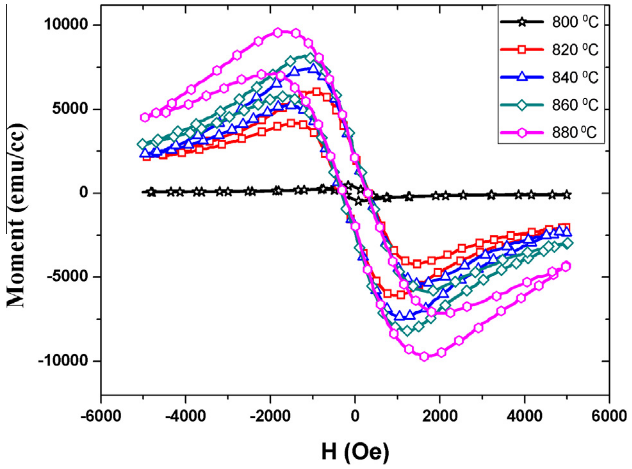

Fig. 6. *M*(*H*) Hysteresis loops at 10 K for annealed films at 800–880 °C.

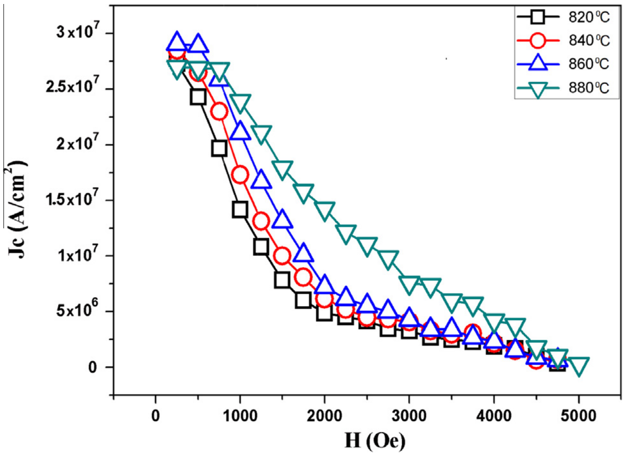

Fig. 7. Critical current densities J_C at 10 K calculated from *M*–*H* loops for annealed films at 820–880 °C.

$$J_C = \frac{60a|\Delta M|}{b(3a-b)}$$

where *a* and *b* are the dimensions of the films and $\Delta M = M_+ - M_-$ is a difference of magnetization values measured in electromagnetic units per cubic.

3.7. Calculations of critical current density

Fig. 7 shows the calculated critical current densities of the films as a function of the applied field, at 10 K. The best J_C value is calculated as 3×10^7 A/cm^2 for a film obtained at 860 °C. It is seen that the J_C values for the film annealed at 860 °C first increase up to 1000 Oe compared to the others; afterwards it starts to decrease for the all the applied field values. It may be argued that the reason for such an abrupt decrease is the presence of large amounts of pores between the grains within the film texture. These pores behave like a defect and create a field dependent effect within the vortex region.

4. Conclusion

In this study, we have investigated the structural and superconducting properties of BSCCO thin films grown on MgO (100) single crystal substrates by using the pulsed laser deposition (PLD) technique. Then we have applied post-annealing heat treatments on those films in order to determine the optimum annealing temperature to improve their quality. In this way, the quality and the superconducting properties of the film exhibited a significant improvement. The films were initially deposited on the substrate at a temperature of 600 °C, and then post-annealed at various temperature intervals. These ranged from 800 to 880 °C in argon and oxygen (Ar: 93, O_2: 7) atmosphere. We have obtained the optimum annealing temperature as 860 °C, resulting in the majority of Bi-2212 superconducting phase, highly textured and *c*-axis oriented perpendicular to the plane of the MgO (100) substrate. The T_Cs were obtained as 42, 75, 76, 82 and 80 K, for annealing temperatures of 800, 820, 840, 860, and 880 °C, respectively.

Acknowledgements

This work is supported by Research Fund of Cukurova University, Adana, Turkey, under Grant No. FEF2011D20. The authors gratefully acknowledge the Material Research Center of Izmir Institute of Technology, for their kind help and to the staff members of the Pulsed Laser Deposition Laboratory for the preparation and analysis of our films.

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