The effects of the post-annealing temperature on the growth mechanism of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ thin films produced on MgO (100) single crystal substrates by pulsed laser deposition (PLD)

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**A B S T R A C T**

The effects of post-annealing temperature were investigated on Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_{8+\delta}$ thin films deposited on MgO (100) 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 ≈ 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 $3 \times 10^7$ A/cm$^2$ for the film annealed at 860 °C.

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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$_2$Sr$_2$Ca$_n$–$x$Cu$_n$O$_{2n+1}$ ($n = 1, 2, 3$) 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 (100) single crystal substrates by pulsed laser deposition.

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2. Experimental

The Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8+$ target was prepared via conventional solid state reaction. The Bi$_2$O$_3$, 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$_2$Sr$_2$Ca$_2$Cu$_2$O$_8+$ were deposited onto MgO (100) 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 ~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 having a rectangular shape.

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 the main matrices.

3.4. Magnetic properties

The DC magnetization measurements of all films are given in Fig. 4. The $T_c$ values 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 860 °C exhibits mainly the low temperature phase (Bi-2212). 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$_2$Sr$_2$Ca$_2$Cu$_2$O$_8+$ target.
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 ($\Delta T$) 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 $T_c$.

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. 2. SEM images of the films annealed at 860, and 880 °C.](image)

![Fig. 3. AFM images of the film annealed at 860 °C.](image)

![Fig. 4. DC magnetic moments versus temperature in 50 Oe ZFC modes for annealed films at 800–880 °C.](image)

![Fig. 5. $R-T$ measurements of the films annealed 860, and 880 °C.](image)
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%, O₂: 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 Tc's were obtained as 42, 75, 76, 82 and 80 K, for annealing temperatures of 800, 820, 840, 860, and 880 °C, respectively.

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