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Growth of superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ thin film using sedimentation method with KCl

B.D. Villaflor*, J.I.L. Bugante, R.V. Sarmago

National Institute of Physics, University of the Philippines, Diliman, Quezon City, Philippines 1101

Abstract

Previous studies have shown that high-quality Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) films can be grown via sedimentation with subsequent post heat treatment [1]. However, as the films were made thinner, relaxation and island formation occurs. To address the problem, we added 10% KCl in the sediment to aid in the melting of the Bi-2212 with subsequent melt-quenching and annealing. The resulting film has a highly c-oriented Bi-2212 crystal structure, has smooth surface, and uniform substrate coverage. The thickness of the film ranges from 490 nm – 540 nm. The highest $J_c$ that was achieved is 3579.54 A/cm$^2$ at 30K, with $T_c$-onset = 85.1K.

Keywords: 74.78.-w Superconducting films and Superconducting low dimensional structures; 61.05.cp X-ray diffraction in crystal structure; 68.37.-d Microscopy of surfaces; thin films

1. Introduction

Fabrication of BSCCO superconducting film has been a topic of intensive research in the last decades since its discovery [2]. Its critical temperature being higher than the boiling temperature of liquid nitrogen (77K) and relatively safe chemical precursors makes it attractive for thin film growth for power application and Josephson junction based devices. Among the three superconducting compounds of BSCCO family (namely Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$, $n=1, 2, 3$) Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) is the most popular material for superconducting thin film synthesis because it has large window of formation [3], relatively high critical temperature and critical current density. Several well-studied deposition methods like Molecular Beam Epitaxy (MBE) [4], and Pulsed Laser Deposition [5], has been used to produce superconducting Bi-2212 high-quality thin film. However, these growth techniques require sophisticated setup like vacuum systems and plasma generation. A novel deposition technique called sedimentation [1] produces quality superconducting Bi-2212 thick films through subsequently subjecting films in liquid phase sintering and annealing process. Among the popular thin film deposition techniques, sedimentation deposition method has the simplest setup and process which makes it attractive for future industrial application. Sedimentation was used to deposit thick Bi-2212 film [1], however, thinner films should be synthesized for future device microfabrication process. Thinner films can be deposited by lowering the density of the Bi-2212 powder suspension. To avoid density limitation during heat treatment, potassium chloride (KCl) can be used to assist film growth. KCl is well known as flux for growth of single crystal Bi-2212 films [6,7]. For the purpose of this study, minute amount of KCl will be used to assist films deposited via sedimentation process with subsequent heat treatment. Crystallinity, surface morphology, and electrical properties of films grown by this method will be studied through several characterization methods.
2. Methodology

Superconducting Bi-2212 powders were prepared using conventional solid-state reaction method. Stoichiometric amounts of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, and CuO precursor powders were ground, pressed and annealed at 837°C for 20 hours with subsequent regrinding and pressing. In the final stage the superconducting powders were reground with 10 wt% potassium chloride (KCl) for 1 hour. To prepare the sedimentation batch, 0.01 grams of the Bi-2211-KCl mixture was homogenized in an agate mortar and pestle and suspended in acetone. The suspension was poured into a beaker containing a MgO (100) substrate. The areal density (amount of powder per unit area of beaker base) of deposition is $1.12 \times 10^{-3}$ g cm$^{-2}$. The suspension was left in ambient air until the powder settled and all the acetone evaporated. The air-dried sample was then withdrawn from the beaker and subjected to a two-part heat treatment process: melt-quenching and annealing process. Several sediment-deposited films were used to optimize the melt-quenching heat profile. All samples were melted for 10 minutes at various temperatures ranging from 900°C to 970°C. The samples were then examined using X-ray diffractometry (XRD) to determine the quality of Bi-2212 formed. The surface of the film with optimal heat profile was examined through scanning electron microscope (SEM). After optimization of melt-quenching heat profile, samples were annealed at 800°C at different duration. The transport properties of annealed films were then examined.

3. Results and discussion

3.1. Effect of KCl on surface morphology of Bi-2212 film after melt-quenching

![Figure 1 SEM image of Bi-2212 film surface melt-quenched in ambient air. (a) Surface of pure Bi-2212 film melt-quenched at 950°C for 10 minutes (b) Low-magnification image of film melt-quenched at 950°C for 10 minutes showing substrate coverage (c) Surface of Bi-2212 film melt-quenched with 10 wt% KCl at 950°C for 10 minutes (d) Low-magnification image of film melt-quenched with 10 wt% KCl at 950°C for 10 minutes](image)

The surface morphology of pure Bi-2212 (without KCl) thin film deposited using the sedimentation with subsequent melting at 950°C for 10 minutes then quenching is shown in figure 1a and 1b. This particular film has a much lower area density than previously studied [1] thus deposits much thinner Bi-2212 film. The surface of the film shows small and fused grains. No apparent grain boundaries can be observed. Some parts of the edge of the substrate are not covered, as seen in the high-contrasting, charged regions in figure 1b. The contrast of the surface is also not uniform, which may indicate uneven surface coverage. Figure 1c and 1d shows the SEM surface image of the Bi-2212 film melted using the same parameters used to produce the film in figures 1a and 1b, but with added 10 wt% KCl prior to film deposition. Compared to the pure Bi-2212 film, the surface of the Bi-2212 film with KCl is smoother, as seen in figure 1c. The grains are much larger and flatter than pure Bi-2212 film counterpart. Growth of calcium-rich, 5-μm sized, spherical facets are also observed, which are seen in other films synthesized using different methods [8]. Full substrate coverage was achieved when KCl was added in film growth, as seen in figure 1d. However, uneven surface can be seen as some areas are darker than the other. No other morphological facets were observed that are peculiar to KCl.

The characteristics observed in pure Bi-2212 thin film indicate a rough surface, which make it unsuitable for device applications [9]. Addition of KCl to the film synthesis not only improved the smoothness of the film, but also the film coverage. This is due to a significant reduction in the viscosity of the melt because of KCl addition. Since KCl has lower melting temperature, it dissolves the Bi-2212 and disperses the powder, as KCl flux does in single crystal growth. The reduction of the viscosity of the melt weakens the grain-to-grain attraction causing the solution to readily spread. Since there is only a small amount of KCl added, the process time is sufficient to evaporate or eventually exclude the flux from the film. EDX measurements do not show the presence of remnant KCl after the film has grown.
3.2. Optimization of melt-quenching profile for growth of Bi-2212 film with 10 wt% KCl

To optimize melt-quench heat profile, several samples were melted for 10 minutes at different temperatures and subsequently quenched in ambient air. Figure 2a shows the normalized XRD plot of films under different melting temperatures. Graph I, II, III and IV corresponds to film melted at 900°C, 925°C, 950°C and 970°C, respectively. The indexed peaks correspond to crystallographic planes of Bi-2212, while the high intensity peak between 2θ = 40° and 45° is due to the MgO (100) substrate. As the melting temperature increases, more Bi-2212 00l peaks appear. Some of the Bi-2212 peaks also increase in intensity as melting temperature is increased. Along with Bi-2212 phase formation, Bi-2201 00l peaks (marked by inverted triangle) can also be observed starting from 925°C melting temperature. But at 970°C, the (002) and (006) Bi-2201 peak vanish, while the intensity of (004) Bi-2201 peak is significantly reduced. The unknown peaks (marked by asterisk) also vanish when film were melted and quenched from 970°C. Since the Bi-2212 film melted at 970°C (plot IV) has highly c oriented Bi-2212 growth, has almost no secondary and unknown phase formation, the process was chosen as a candidate melt-quench profile.

Figure 2b and 2c shows the SEM image of the Bi-2212 film melted with KCl using the chosen melt-quench profile. Compared to pure Bi-2212 film and Bi-2212 film melted with KCl at 950°C in figure 1, the surface of the Bi-2212 film with KCl using the optimized melt profile shows a very smooth morphology as seen in figure 2b. The surface of the film is composed of large, flat, and continuous grains which are separated by grain boundaries. Furthermore, full substrate coverage is also achieved using the optimized melt-quench profile as seen in figure 2c. No island formation and uneven surface features can be observed.

3.3. Transport properties of Bi-2212 films with KCl annealed at different duration

Resistance vs. temperature measurements of melt-quenched Bi-2212 film with KCl (as prepared) showed T_c-onset ~ 40 K. This transition temperature is very low for Bi-2212 thus post heat treatment is essential. The measured thickness of the film annealed at different duration ranges from 490 nm ~ 540nm. Figure 3a shows the normalized resistance vs. temperature behaviour of melt-quenched Bi-2212 films with KCl, annealed at 800°C for 10 hours (circle), 15 hours (inverted triangle), and 20 hours (triangle). All the samples showed superconducting transition with T_c-onset = 83.5K, 85.7K, 85.1K for sample annealed for 10 hours, 15 hours, and 20 hours, respectively. The increase of T_c-onset after annealing can be attributed to an increase of oxygen content of sample while it is being annealed in ambient air which in turn increases carrier concentration [10]. It can also be seen from figure 3a that the transition width of film annealed for 20 hours (ΔT = 16.1K) is larger than transition width of films annealed for 10 and 15 hours (ΔT = 8.1K and 8.6K, respectively). The increase of transition width might indicate significant changes in oxygen vacancies [11], which was not controlled in this case since the samples were annealed in ambient air.

The current-voltage (IV) characteristics of the three samples were also examined at different magnetic field strength for critical current density (Jc) computation. Figure 3b shows the representative current versus voltage plot for film annealed for 15 hours. The chosen voltage criterion for Jc computation for all of the samples is V_c = 0.05V, which
Figure 3. Transport properties of Bi-2212 film melt-quenched with KCl at 970°C for 10 minutes, annealed at 800°C at different duration (a) Normalized resistance vs. temperature behaviour of the film annealed for 10 hours (circle), 15 hours (inverted triangle), and 20 hours (triangle) (b, c, d) Critical current density vs. temperature behaviour at different magnetic field strength for film annealed for (b) 10 hours, (c) 15 hours, (d) 20 hours

is the horizontal line in figure 3b. All films exhibited the similar I-V characteristic patterns. The sudden appearance of voltage after applying current greater than their critical current is attributed to flux flow [12].

Figures 1c, 1d, and 1e shows the variation of $J_c$ with temperature at different applied magnetic field strength for films annealed for 10, 15, and 20 hours, respectively. The critical current $I_c$ at 30 K (self-field) of films annealed at 10 hours, 15 hours, and 20 hours are 3.99 mA, 3.87 mA, and 4.74 mA, respectively. By knowing the thickness of the films (490 nm – 540nm), the cross-sectional area was solved and the critical current density ($J_c$) was computed. The Bi-2212 film annealed at longer duration showed the highest $J_c$ (3579.54 A/cm²), while the film annealed for the shortest time showed the lowest $J_c$ (2038.83 A/cm²). This may indicate that at longer annealing duration there is a significant increase in grain boundaries or defects which can serve as additional pinning sites on the film. Increase in $J_c$ was also observed when magnetron reactive sputtered film was subjected at longer annealing time [13].

4. Conclusion

Surface morphology of the Bi-2212 film improved upon addition of 10 wt% KCl in film growth. The optimized melt-quenching heat profile showed a highly c-oriented crystal, with almost no secondary phase growth. The surface of the melt-quenched film showed a much smoother surface than the film melt at lower temperature (figure 1c, 1d and figure 2b, 2c). Melt-quench films show low $T_c$-onset (~40K) thus films were post-annealed. The thickness of post-annealed film ranges from 490 nm – 540nm. The $J_c$ of the samples increases as duration of annealing increases. The highest $J_c$ that was observed at 30 K is 3579.54 A/cm² with $T_c$-onset = 85.1K.

References