Preparation of c-axis textured Bi-2212 thin films on silver substrates by using chemical solution deposition

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Abstract. The silver sheath material plays an important role in the preparation of Bi-2212 and Bi-2223 tape conductors. In this paper, a chemical solution deposition method was proposed to fabricate the Bi-2212 thin film on Ag substrates after polishing and annealing. The influences of the sintering temperature were investigated. After sintered at 780 °C or 790 °C for 5 h in 8% O₂ (N₂ balanced), samples with almost pure and highly c-axis textured Bi-2212 phase were prepared. And the full width at the half maximum (FWHM) value of the rocking curves for the Bi-2212 (0012) plane reached below 5.8°.

1. Introduction
High temperature superconductor Bi₂Sr₂CaCu₂O₈ (Bi-2212) still merits a great attraction for its high critical current density in a high magnetic field at 4.2 K [1]. And because of its intrinsic Josephson effects, Bi-2212 is one important candidate to realize solid-state sources of tera hertz (THz) radiation [2]. Bi-2212 thin films were successfully fabricated by several methods, such as chemical vapor deposition (CVD) [3], pulsed laser decomposition (PLD) [4], molecular beam epitaxy (MBE) [5], sputtering [6] and metal-organic deposition [7, 8]. It is found that Ag substrate is effective to produce highly textured Bi-2212 microstructures [9, 10], and it can lower the solidification temperature of Bi-2212 [9]. In this study, the Bi-2212 thin film was prepared on Ag substrate by using the chemical solution method. The influences of the sintering temperature on phase assemblage, surface morphology, and the c-axis texture of Bi-2212 thin films were investigated.

2. Experimental
Silver substrates with the size of 5 mm × 5 mm were cut from a silver tape of 0.4 mm in thickness. After pressed at 90 MPa to obtain a flat surface, the silver substrates were annealed at 300 °C in pure N₂ for 30 min to release stress. Then all samples were mechanical polished by 1 μm diamond suspension. Finally, the silver substrates were ultrasonic cleaned in acetone for 8 min and alcohol for 5 min.

The solution preparation followed the same procedure proposed by Tanaka [11]. The starting compositions Bi(NO₃)₅H₂O, Sr(NO₃)₂, Ca(CH₃COO)₂·H₂O and Cu(CH₃COO)₂·H₂O were
weighed to ensure that the molar ratio of Bi, Sr, Ca and Cu was 2:2:1:2. The pH value was adjusted to 5.5 by adding ammonia water (28%). The solution was stirred at 60 °C for 2 hours and stirred at 90 °C for 1 hour. Finally, 9 mL of the solution was refined under decompression at 45 °C for half an hour. The molar concentration of total metal ions was 0.59 mol/L.

The obtained solution was spin-coated on as prepared Ag substrate with 6000 rpm for 80 s. After dried at 70 °C for 2 min, the obtained sample was pyrolyzed in air at 400 °C for 5 h. The spin-coating and pyrolysis processes were repeated 6 times in total. Finally, the samples were sintered at different temperatures ($T_s$) from 730 °C to 850 °C under 8% O$_2$ (N$_2$ balanced) for 5 h. The temperature ramping rate of all heating and cooling processes is 200 °C/h.

The thermal stability of the chemical solution was investigated by thermogravimetric and differential scanning calorimeter (TG-DSC) with a heating rate of 10 °C/min up to 900 °C in air. An optical microscope (Nikon DXM1200) was used to observe the surface morphologies of pyrolyzed films. The X-ray diffraction (XRD) patterns and rocking curves for the Bi-2212 (0012) plane were measured by X-ray diffractometer (Rigaku, D/max 2500 V, Cu Kα). The surface morphologies of thin films were observed by a scanning electron microscope (SEM) of LEO 1530 SEM, equipped with an energy-dispersive X-ray spectroscopy (EDX) detector.

3. Results

Fig. 1 shows the TG-DSC curves of the chemical solution. Two abrupt weight losses appeared at 260-360 °C and 370-460 °C in TG curve, accompanied by two exothermic peaks at about 340 °C and 425 °C in DSC curve. Another abrupt weight loss occurred at 530-600 °C in TG curve, with an endothermic peak at about 575 °C in DSC curve.

![Figure 1. TG-DSC curves of the solution. Solid line for the mass curve and dashed line for the DSC curve.](image)

The optical images of selected pyrolyzed samples are shown in Fig. 2. Blank zones appeared in the sample after only one time coating, as shown in Fig. 2 (a). The blank zones are quite large, with an average size of about 50 μm. After 6 times repeated spin-coating and pyrolysis processes, the surface became much more homogeneous, as shown in Fig. 2 (b).

![Figure 2. Optical microscope images of pyrolyzed films, (a) after one time coating, (b) after 6 times coating.](image)

Fig. 3 shows the XRD patterns of the samples sintered at different temperatures (730 °C to 850 °C) in 8% O$_2$ (N$_2$ balanced) for 5 h. The diffraction peaks of the Bi-2201 phase can be observed in almost all samples, especially in case of high sintering temperature. Almost pure Bi-2212 phase is formed at 780 °C and 790 °C. According to XRD patterns, the volume fractions of Bi-2201 and Bi-2212 phase can be calculated by equation (1) and (2),

$$f_{2201} = \frac{I_{(006)}^{2201}}{I_{(006)}^{2201} + I_{(008)}^{2212}} \quad (1)$$

$$f_{2212} = \frac{I_{(008)}^{2212}}{I_{(006)}^{2201} + I_{(008)}^{2212}} \quad (2)$$
where \( f_{2201} \) and \( f_{2212} \) represent the volume fractions of Bi-2201 and Bi-2212 phase respectively, 
\( I_{(006)}^{2201} \) and \( I_{(008)}^{2212} \) represent the intensities of Bi-2201 (006) peak and Bi-2212 (008) peak respectively.

**Figure 3.** X-ray diffraction patterns of samples at different sintering temperature.

**Figure 4.** The volume fraction of Bi-2201 and Bi-2212 phases as a function of sintering temperature.

The calculated volume fractions of the Bi-2212 and Bi-2201 phases with different sintering temperature are shown in Fig. 4. \( f_{2212} \) reached maximum at 780 °C and 790 °C. It decreased rapidly at above 810 °C. The Bi-2201 phase became the main phase at this temperature region.

Fig. 5 shows the surface morphologies of selected samples sintered at 730 °C, 780 °C, 820 °C and 850 °C, respectively. The grain size increased with increasing sintering temperature. A needle sharp phase appeared at 850 °C, as shown in Fig. 5 (d). This needle phase seems to be Cu free according to the EDX measurement. The molar ratio of Bi, Sr and Ca is close to 9.0 : 12.4 : 6.6.

**Figure 5.** SEM images for BSCCO thin films sintered at (a) 730 °C, (b) 780 °C, (c) 820 °C and (d) 850 °C, respectively.

**Figure 6.** Full width at the half maximum (FWHM) of the rocking curves for the Bi-2212 (0012) plane as a function of the sintering temperature.

The FWHM values of the rocking curves for samples with different sintering temperature (\( T_s \)) are shown in Fig. 6. It decreased with increasing \( T_s \) in general. The minimum value reached
5.3° at 800 °C to 820 °C, which showed a nice c-axis texture. But the FWHM value increased rapidly when $T_s > 830 °C$, corresponding to the formation of large amount of the Bi-2201 phase.

4. Discussion
Blank zones appeared on the film which was spin-coated and pyrolyzed only once (Fig. 2 (a)). The low wettability of the solution for Ag substrate and a relatively fast heating rate (200 °C/h) might be the reasons. For the low wettability led to the shrink of the film during the pyrolysis process and a fast heating rate caused bubbles of big size. Both the shrink of the film and the bubbles gave rise to the blank zones. After repeated coating and pyrolyzing, the blank area was covered by new layers, leading to a comparatively smooth surface (Fig. 2 (b)).

Almost pure Bi-2212 phase was formed when sintering temperature was 780 °C or 790 °C, which was lower than the common solidification temperature for Bi-2212 thin film [7, 8]. It is because that silver can lower the solidification temperature of Bi-2212 [9] and low oxygen pressure decreases the melting point of Bi-2212. Below 780 °C, Bi-2201 phase still existed after the sintering process of 5 hours. For Bi-2201 phase is stable at low temperature [12]. Above 790 °C, Bi-2201 phase and a new phase appeared as second phases. This new phase showed a relatively strong intensity in the XRD patterns when sintering temperature was 850 °C (See the marked unknown phase in Fig. 3). Baker [13] has reported that the decomposition of Bi-2212 leads to the appearances of some new phases including Bi$_9$Sr$_{11}$Ca$_5$O$_y$. Its major diffraction peaks are near the angle 30° 2θ. And the peak of the unknown phase we observed here located at the angle 30.2° 2θ. So, the unknown phase might be Bi$_9$Sr$_{11}$Ca$_5$O$_y$ and it was due to the decomposition of Bi-2212 phase. Further study is needed to identify this interpretation.

5. Conclusion
We have successfully fabricated almost pure Bi-2212 thin film on Ag substrate by a chemical solution deposition method. Blank zones on the pyrolyzed film will disappear after repeating the spin-coating and pyrolysis processes for 6 times. The sintering temperature for pure Bi-2212 phase is 780 °C or 790 °C. It is lower than the common solidification temperature for Bi-2212 because of Ag substrate and low oxygen pressure. For the film sintered at 780 °C, rocking curve shows that the FWHM of Bi-2212 (0012) reflection is 5.8°.

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