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Growth of Bi-Sr-Ca-Cu-O ribbon-like thin films on Ag substrates

Yoshimasa Satoh,[a,b,c,*] Shunichi Arisawa,[b,c] Akihiro Fukuyo,[b,d]
Yoshihiko Takano,[b,c] Akira Ishii,[b] Takeshi Hatano,[b,c,d] Kazumasa Togano[a,b,c]
[a] University of Tsukuba, Institute of Materials Science, [b] National Research Institute for Metals,
[c] CREST, Japan Science and Technology, [d] Science University of Tokyo, Faculty of Science and Technology
*National Research Institute for Metals, 1-2-1, Sengen, Tsukuba-shi, Ibaraki 305-0047, Japan.
Fax: 81-298-59-2301, e-mail: satoh@nrim.go.jp, SATOH.Yoshimasa@nims.go.jp (On and after April 1, 2001)

The melt growth process of $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (Bi-2212) ribbon-like thin films on Ag substrates has been studied. Ag tapes, Ag single crystals and sputter-deposited Ag films were used for this process. Studies on textures and morphology of the Ag substrates were carried out. The ribbon-like thin films grew on the Ag substrates that lost their flatness after heat treatment. The results of this investigation provided valuable suggestions for revealing growth mechanisms of ribbon-like thin films. That is, the structure and growth of ribbon-like thin films were predominantly determined by Ag substrate morphology.

Key words: Superconductor, $Bi_2Sr_2Ca_1Cu_2O_x$, Thin film, Ribbon-like, Ag

1. INTRODUCTION

Since the discovery of the Bi-based high-T_c superconductors by Maeda *et al.* [1], a lot of investigation on various methods for synthesizing thin films has been carried out [2-10]. The Bi-based superconductors must be synthesized in the form of high quality thin films for electronics applications, especially for intrinsic Josephson junction devices. However, the common techniques to synthesize oxide superconducting films [2-9] require highly sophisticated vacuum apparatuses. Furthermore, Bi-based high-T_c thin film fabrication is difficult to reproduce even with such pieces of equipment.

Growth of superconducting $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (Bi-2212) ribbon-like thin films through melt processing has been found on the Ag tapes [11]. With success in synthesizing both Bi-2212/Ag tapes and Bi-2212 single crystals through melting processes, ribbon-like thin films are expected to have high quality superconducting properties and crystal structures. The ribbon-like thin films spread out on the Ag tapes from the region where the Bi-2212 starting material was partially melted and solidified. These ribbon-like thin films stuck firmly to the Ag tapes. Some ribbon-like thin films were as thin as the films synthesized by vacuum deposition techniques. It was confirmed that the major phase of the ribbon-like thin films was a *c*-axis-oriented Bi-2212 phase in spite of the coexistence of other phases. The surface roughness of the Ag tape was a problem for further applications as well.

Many studies on ribbon-like thin films were carried out after the discovery. *In situ* observation of the growth of ribbon-like crystals [12-15], suggestions of growth model [14], and selective growth on Ag [15].

The synthesis process of the ribbon-like thin films does not need any of the expensive equipment mentioned above. However, the growth mechanism of the ribbon-like thin films is not concretely understood, nor has the synthesis condition been entirely optimized.

In this paper, we present a study of Bi-2212 ribbon-like thin films on three kinds of Ag substrates (Ag tape, Ag single crystal, and sputter-deposited Ag film on single crystal MgO (001)) by using Bi-2212 pellets. Structure and the effects of the Ag substrates on growth of ribbon-like thin films were studied. Structural analyses of the ribbon-like thin films were performed. The results provide a suggestion of growth mechanism of ribbon-like thin films.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Ag substrates

Ag substrates are used in the process of ribbon-like thin film fabrication. In this study, three kinds of Ag substrate were prepared: (a) Ag tape (50 μm thick): It is commercially sold and generally used in fabrication of Bi-2212/Ag tape conductors. As received Ag tapes were washed in an ultrasonic cleaner with acetone. (b) Ag single crystal: Commercially available polished ones were used. (c) Sputter-deposited Ag film on MgO (001): Ag films on MgO (001) substrate were prepared by an RF-magnetron sputtering apparatus. The size of the MgO substrate was $15 \times 15 \times 0.5mm^3$. 99.99% pure Ag target was 100mm in diameter. The distance between the MgO substrate and the Ag target was 45.5 mm. Process gas was 99.999% pure Ar. The base pressure was 2.0×10^{-5} Pa. In the sputtering process, the MgO substrate was not intentionally heated during the deposition process in order to induce the two-dimensional growth [16]. Below 100°C, Ag films grow on MgO (001) in Frank-Van der Merwe growth mode [17]. That is, two-dimensional film growth is expected to form a flat Ag surface. To clean the surface of MgO, reverse sputtering was performed for 10 minutes prior to the Ag deposition. The Ar gas pressure and the inlet power for reverse sputtering were 2.0 Pa and 85 W, respectively. The condition of presputtering (sputtering with the shutter closed) is as follows: RF power = 79W, processing pressure=2.0Pa, time=10min. Sputter deposition was performed at an RF power of 79W and a processing pressure of 2.0Pa, which produced Ag films that were deposited with the 11 Å/sec. This was the smallest deposition rate possible with our apparatus. Sputter deposition was carried out until the Ag film was

3.0 μm thick.

Before and after heat treatment, the texture and morphology of the Ag substrates without putting a Bi-2212 pellet on the Ag substrates were characterized by X-ray diffraction (XRD) analysis and Atomic Force Microscopy (AFM), respectively.

Since the processing temperature (~900°C max.) is close to the melting temperature of Ag (961.78°C), the surface roughening must be noted. The roughening derived from the heating. Root-mean-square (RMS) surface roughness of as-prepared (-deposited) and as-annealed Ag substrates was quantitatively evaluated by AFM.

2.2 Ribbon-like thin film fabrication

The fabrication method for the ribbon-like thin films is indicated in Fig. 1. Sintered Bi-2212 pellet was put in the center of a Ag substrate. The substrate with the pellet was then put in a tube furnace and heated at the maximum temperature T_{max}~900°C in the flowing O_2 at 100 sccm of ambient pressure. Figure 2 shows a heat treatment schedule for the growth of ribbon-like thin films. After this process, ribbon-like Bi-Sr-Ca-Cu-O thin films sticking to the Ag substrate are found around the solidified starting material. The ribbon-like thin films were observed with an optical microscope. For experimental measurements, the area of ribbon-like thin films sticking to the Ag substrate was cut out (That is, the cutout included the ribbon-like thin films, the Ag substrate, but the droplets of starting material were excluded). Structural analyses of the ribbon-like thin films were performed by XRD.

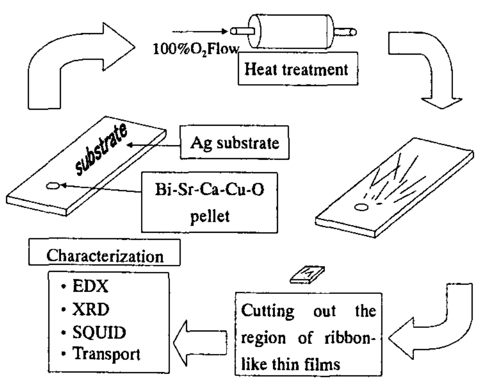

Fig. 1. Fabrication process of Bi-Sr-Ca-Cu-O ribbon-like thin films.

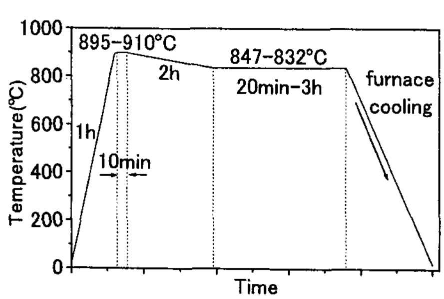

Fig. 2. Heat treatment schedule for ribbon-like thin film fabrication.

3. RESULTS AND DISCUSSION

3.1 Texture and morphology of the Ag substrates

The XRD patterns of the as-prepared (-deposited) Ag substrates were presented in Fig. 3. As shown in Fig. 3(a), Ag grains with several textures coexisted in the Ag tape substrate. It was confirmed that Ag (001) texture was formed in both (b) single crystal and (c) sputter-deposited film.

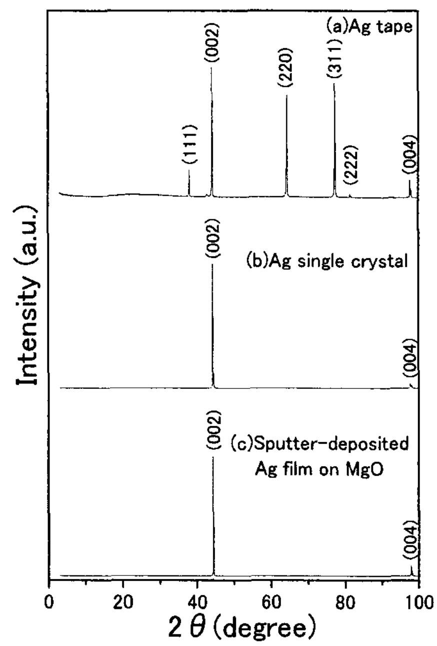

Fig. 3. XRD patterns of Ag substrates. (a) Ag tape, (b) Ag single crystal, and (c) sputter-deposited Ag film on MgO.

The RMS surface roughness of the as-prepared (-deposited) and as-annealed Ag substrate was studied. Heat treatment was the same as the ribbon-like thin film fabrication process (shown in Fig. 2). Heating was carried out in Ag substrates without Bi-2212 pellet. The RMS values provide quantitative evaluation of surface roughness. Each RMS value is presented in Table I. In the case of Ag tape and single crystal, the roughening of the Ag surface due to annealing was significant. Although the RMS value of sputter-deposited Ag film increased after heating, it was far less than those of the Ag tape and the single crystal. Flat surface of sputter-deposited Ag film is desirable for applications in electronics.

	As-prepared (-deposited)	As-annealed
Tape	~300nm	~1000nm
Single crystal	~200nm	~800nm
Sputter-deposited	1.5nm	35nm

Table I RMS surface roughness of the Ag substrates.

3.2 Growth and structure of ribbon-like thin films

The Bi-Sr-Ca-Cu-O ribbon-like thin films on the Ag substrates exhibited different appearances. The micrographs of Ag substrates were presented in Fig.4 (a) Ag tape, (b) Ag single crystal, and (c) sputter-deposited Ag film on MgO. Ribbon-like thin films grew on both the tape and the single crystal substrate. On the contrary, the ribbon-like thin films did not grow on sputter-deposited Ag film. As shown in Fig. 4 (a), grain boundaries appeared in the Ag tape. There was no grain boundary in the Ag single crystal as presented in Fig. 4 (b). Surface roughening was observed with an optical microscope in both the Ag tape and the Ag single crystal. Especially for the ribbon-like thin films on the Ag single crystal, forming some cracks was observed. This is a mechanical problem on ribbon-like thin films formed on single crystal Ag. It is also confirmed with the optical microscope that surface of the sputter-deposited Ag film was considerably flat even after heat-treated.

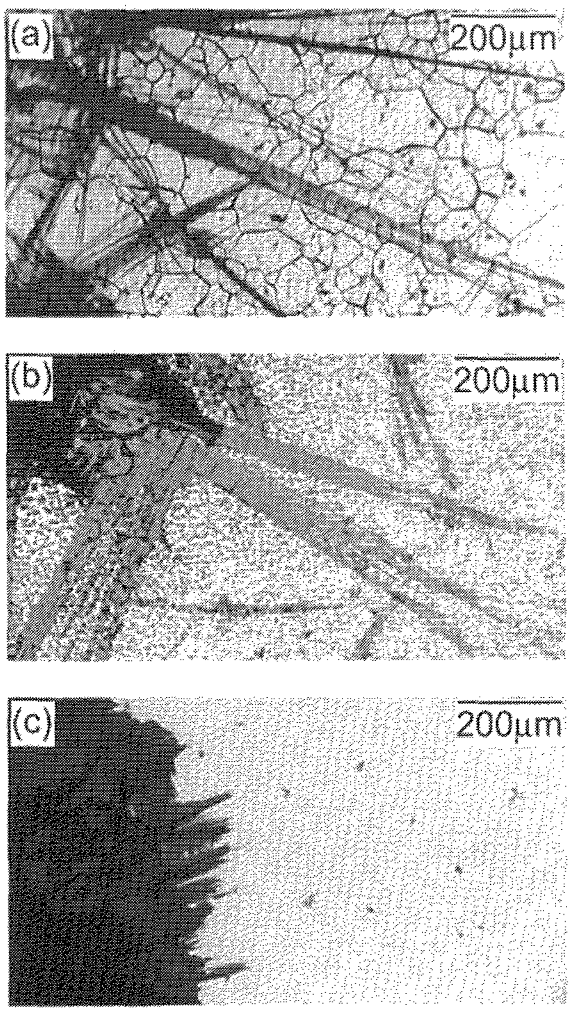

Fig. 4. Optical micrographs of each Ag substrate surface after a heating process. (a) Ag tape, (b) Ag single crystal, (c) sputter-deposited Ag film on MgO.

The XRD patterns of the ribbon-like thin films were presented in Fig. 5. All the measurements were carried out in the area without droplet of starting material. On the Ag tape, *c*-axis-oriented Bi-2212 thin films were synthesized in spite of the coexistence of the $Bi_2Sr_2Cu_1O_y$ (Bi-2201) and Bi_2SrO_4. Bi-2201 and Cu-free phases were synthesized on the Ag single crystal, but there exists no Bi-2212 phase. On the sputter-deposited Ag film, although there was no ribbon-like thin film, the existence of transparent Cu-free phase on the Ag film was confirmed.

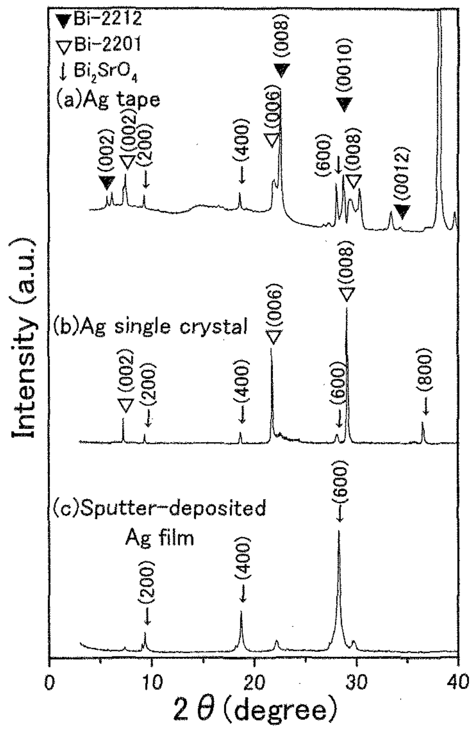

Fig. 5. XRD patterns after heating for ribbon-like thin film fabrication. (a) Ag tape, (b) Ag single crystal, (c) Sputter-deposited Ag film on MgO. No ribbon-like thin films grew on the sputter-deposited Ag film. Peaks of the Cu-free phases were detected on the Ag film (melted and solidified starting material was excluded).

It was clarified that Ag substrate morphology rather than texture of Ag substrate was one of the key factors of ribbon-like thin film growth. However, superconducting thin film fabrication on flat sputter-deposited Ag films is expected for electronics applications. Ribbon-like thin film fabrication on extremely flat Ag film is under investigation. Research regarding the fabrication process for electronics technology applications will be published elsewhere.

4. SUMMARY

Bi-Sr-Ca-Cu-O ribbon-like thin films were fabricated on various Ag substrates. That is, Ag tape, Ag single crystal, and sputter-deposited Ag film were used as the substrates for studying the effect of the Ag substrates on ribbon-like thin film growth. Growth of ribbon-like thin film was promoted especially rough Ag substrates. The results provided valuable suggestions for revealing growth mechanisms of ribbon-like thin films. The structure and growth of ribbon-like thin films were predominantly determined by substrate morphology.

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