Anisotropy of Bi-Sr-Ca-Cu-O Thin Film Growth

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ABSTRACT

The growth mechanism of the superconducting Bi-Sr-Ca-Cu-O thin films were examined. The films were fabricated on Y3Al5O12(YAG) single crystal substrates by metalorganic chemical vapor deposition (MOCVD). The microstructure of the film was investigated by atomic force microscopy (AFM) and cross-sectional high-resolution transmission electron microscopy (HREM). The anisotropic growth were observed in this film. The modulated structure of Bi-Sr-Ca-Cu-O thin films makes the main contribution to this anisotropic growth.

KEYWORDS: BiSrCaCuO thin films, growth mechanism, modulated structure, anisotropic growth

INTRODUCTION

The superconducting properties are strong depend on the growth process, which are controlled by growth mechanism. So, to understand the crystal growth mechanism is very important terms for fabricating a high-quality superconducting material. The growth mechanism of Bi-Sr-Ca-Cu-O thin films prepared by several fabricating technique had been investigated. Two-dimensional growth with a growth unit of approximately 15Å was observed by reflection high energy electron diffraction (RHEED) intensity variations[1]-[3]. In comparison to Y-Ba-Cu-O films, the Bi-Sr-Ca-Cu-O 2201 films tend to grow only in the form of layer-by-layer growth[4]. We also observed 15Å of the minimum growth unit cell by AFM and HREM[5]. Bi-Sr-Ca-Cu-O superconducting thin films were prepared by MOCVD on YAG(Y3Al5O12) substrate. YAG substrate is suitable for observation of initial growth stage because of its surface smoothness and chemical stability[6]. In this study, the microstructure of this films were observed by means of cross-sectional HREM, and the initial growth stages were observed by AFM, with the object of understanding the growth mode of Bi-Sr-Ca-Cu-O thin films. We proposed a growth model for making clear the reason of anisotropic growth taking account of the modulated structure.

EXPERIMENTAL PROCEDURE

We used a conventional cold-wall type MOCVD apparatus with metalorganic source materials of Sr(DPM)2, Ca(DPM)2, Cu(DPM)2 and Bi(phen). The substrates of YAG(100) single crystal were placed on the Inconel superalloy susceptor and heated up to 800°C by radio frequency induction. We fabricated the films on these substrates with a film deposition rate of 0.2nm/min. at 800°C, followed by cooling down to room-temperature, and no postheating treatment was applied. The total gas pressure in the reactor was 10 torr, and the Oxygen partial pressure was 8.6 torr. The chemical composition ratio of the film and the average film thickness were analyzed by Inductively Coupled Plasma (ICP). The films were characterized by X-ray diffraction(XRD). Cross-sectional high-resolution electron microscope observations were performed using an H-9000UHR transmission electron microscope operated at 300kV for investigating the microstructure of the films. The initial growth stages were observed by AFM.
RESULTS AND DISCUSSION

We fabricated Bi-Sr-Ca-Cu-O thin films of 7Å, 15Å and 2000Å on YAG(100) single-crystal substrates by MOCVD. For the average thickness of 7Å and 15Å, deposition was carried out for 3.5min and 7.5min respectively, at a deposition rate of 2.0Å/min. The chemical composition was Bi: Sr:Ca:Cu=2:2:1:2(2212). We took care to achieve the desired chemical composition to avoid the growth of unwanted phases. XRD patterns of these films showed the c-axis-oriented Bi-Sr-Ca-Cu-O 2212 phase clearly, although the diffraction peaks of the film with 7Å average thickness were broad. The initial growth stage of the Bi-Sr-Ca-Cu-O thin film with the average thickness of 7Å, as observed by AFM is shown in Fig.1. Figure 1 shows the top-view image of the film.

![Fig.1](image1.png)

**Fig.1** The top view image of the 7Å of the average thickness film at the initial growth stage, observed by AFM.

The substrate was not covered perfectly with the film, because the average thickness of 7Å was not sufficient to cover the entire substrate surface with the c-axis-oriented Bi-Sr-Ca-Cu-O 2212 thin film. The dark and flat area in this figure is the substrate surface, and the slightly bright area on the center is the film. The brightest part of the oval shape appearing at all observed area might be due to three-dimensional nucleation, secondary phase grain or the simple contamination, and further detailed investigation of this phenomenon is required. The film was formed into island shape with very flat top surface. The height of island shaped film was measured 30Å from the data of AFM, which is one unit cell of the c-axis-oriented Bi-Sr-Ca-Cu-O 2212. This film also formed rectangle shape in the a-b plane, and the side of b-axis direction is longer than a-axis direction. This feature means anisotropy of crystal growth. Figure 2 shows the top-view of 30Å of the average thickness film. The dark area is the substrate surface, and the slightly bright area is the film. The brightest part of the oval shape still remain. The island shaped film spread and covered 80% of the substrate surface. The height of the film is 30Å, which is same as 7Å of half thickness film in Fig.1. These data show two-dimensional growth. These island shaped films are all rectangle shape in a-b plane, and the side of b-axis direction is very long. It is easy to guess that two-dimensional growth were continued from 7Å to 15Å thickness film. Anisotropic growth also continued. From the results of AFM image, the Bi-Sr-Ca-Cu-O 2212 films tend to grow in the form of two-dimensional growth. The growth rate of b-axis direction(a-c plane) is faster than a-axis direction(b-c plane). These two feature of crystal growth is very important for investigating the growth mechanism.

![Fig.2](image2.png)

**Fig.2** The top view image of the 15Å of the average thickness film at the initial growth stage, observed by AFM.

The reasons of the two-dimensional growth were supposed that the existence of the cleavage plane Bi-O layer seems to be played an important role by some studies. Then, we tried to make clear the reason of this anisotropic growth. We observed a cross-sectional high-resolution structure image of the film of 2000Å thickness is shown in Fig.3. This image projected along the [100] direction and the observation area is approximately 1800Å remote from the substrate surface. No intergrowth and thick defect could be found in this area, and this result indicates the good quality of this film. This image shows a structural modulation with a 27Å period along the b-direction. The modulation period was calculated from the electron diffraction pattern corresponding to the structure image in Fig.3(7).