Submicron-size Fabrication of BSCCO Thin Films by using Patterned Substrates

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***Abstract*—Submicron-size $Bi_2Sr_2CaCu_2O_x$ (BSCCO) structures of mesa patterns with dimensions of 0.3 μm x 0.3 μm and line patterns of 0.3 μm width were fabricated on patterned $SrTiO_3$ (001) substrates. These submicron-sized BSCCO structures were grown on patterned structures directly drawn by an focused ion beam (FIB) apparatus with a Ga ion beam accelerated at 30 kV. The c-axis oriented epitaxial BSCCO thin films were prepared by the molecular beam epitaxy (MBE) method on the patterned substrates with thickness of 70 nm. The fine submicron-size BSCCO structures were obtained from the growth properties of the crystal, which favor the formation of (100), (010), (110) and (1$\bar{1}$0) facets. These patterns are free from damages from various etching processes.**

I. Introduction

High-resolution patterning of high-T_c superconductors is a key technology for developing high-T_c superconducting electronics. A variety of techniques have been developed for patterning high-T_c superconductors, which include chemical etching [1], ion beam sputtering [2]–[4], modification patterning process using ion implantation [5], and laser patterning [6], [7], among others. For submicrometer or nanometer size fabrication, focused ion beam (FIB) [8], [9] and electron beam lithography [10], [11] have been utilized. In most cases, however, damaged parts remain in the films that have been exposed to chemicals or ions, limiting the minimum size of the pattern, and size of pattern is limited to a micron-scale. For integration and improvement of high-T_c superconducting devices, a high-resolution process in a nanometer-scale without damage should be developed.

In the case of semiconductors, especially III-V compound semiconductors, many researchers have directed their efforts to studies on the crystal growth on patterned substrates in order to fabricate quantum structures and quantum devices [12], [13]. Nanometer-sized structures have been obtained by utilizing the facet growth achieved by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD). For high-T_c superconductors, there was few reports on facet growth for the fabrication of nanometer- or submicron-size structures.

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In this paper, we report for the first time the facet growth of submicron-size $Bi_2Sr_2CaCu_2O_x$ (BSCCO) thin film using patterned substrates. BSCCO is known to show well-defined two dimensionality, and to form plate-type single crystals with their a-b planes parallel to the plate, with (100) and (010) facets on the edges. In MBE growth, the features of crystal growth are the same as those of a single crystal. Therefore, we think that BSCCO is a suitable material for this purpose, compared with $YBa_2Cu_3O_y$, which is inclined to grow spirally. A FIB apparatus was used for the patterning of substrates, because it is a direct process that needs no masks or chemicals, and has a resolution of approximately 50 nm.

II. Experimental

Sub-micron structures were fabricated by a procedure as drawn in Fig. 1. BSCCO films were prepared on the patterned substrates etched by the FIB apparatus SMI9200 (Seiko Instruments Ltd.). Ga ion beam accelerated at 30 kV was focused with a spot size of about 50 nm at an 80 pA beam current. Mesa and line patterns size of 0.3 - 2 μm were directly drawn on $SrTiO_3$ (001) substrates. It was found that the $SrTiO_3$ substrates could be etched to 1 μm thickness by a dose of 4.8×10^{18} ions/cm^2.

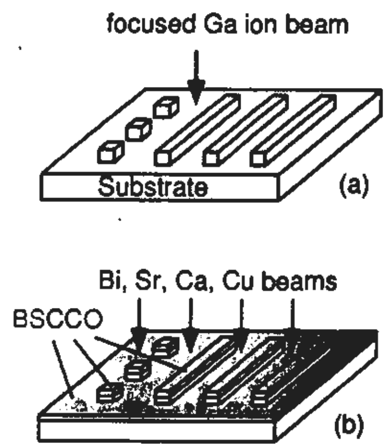

Fig. 1. An process of fabrication of submicron-size BSCCO structures. (a) The patterns are directly drawn by FIB on the substrate. (b) BSCCO thin films are prepared by MBE.

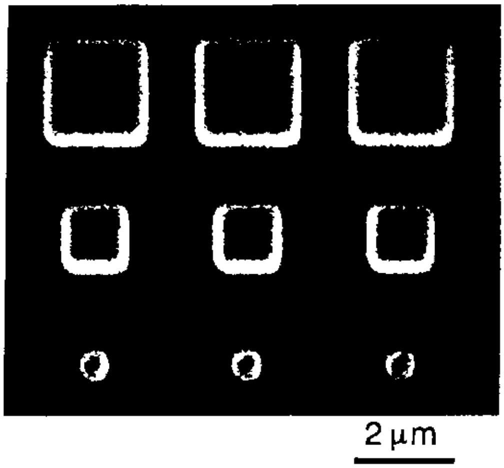

Fig. 2. SIM image of the patterned $SrTiO_3$ substrate. Areas of mesa structures are 2 μm × 2 μm, 1 μm × 1 μm and 0.5 μm × 0.5 μm and the height is 1.3 μm.

BSCCO thin films were prepared by a MBE method with a sequential deposition technique on the patterned $SrTiO_3$ (001) substrates. The growth temperature was 740°C, and the growth rate was 29 nm/h. An oxygen/ozone mixture with an ozone content of ~10% was provided to the substrate at a background pressure of 2.5×10^{-3} Pa. The deposition interruption sequence with a deposition period of 10 s and an interruption period of 60 s was adopted. The details of this method have been reported elsewhere [14],[15].

The structures obtained were observed using Hitachi S-4500 field-emission scanning electron microscope (FE-SEM). Crystal structures were confirmed by *in situ* reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD). Chemical compositions as well as area mappings of thin films were measured by energy-dispersive X-ray microanalysis (EDX).

III. Results and Discussion

Figure 2 shows a scanning ion microscopy (SIM) image of mesa structures fabricated on a $SrTiO_3$ substrate. The sizes dimensions of these mesas are 2 μm × 2 μm, 1 μm × 1 μm and 0.5 μm × 0.5 μm and the height is 1.3 μm. Mesa structures were obtained with less than one submicrometer resolution.

BSCCO thin films were epitaxially grown on patterned $SrTiO_3$ (001) substrates. The XRD pattern showed that the c-axis oriented thin film with c = 3.07 nm was obtained. An epitaxial relationship between the BSCCO thin film and the $SrTiO_3$ (001) substrate was confirmed by *in situ* RHEED. BSCCO thin films grown on $SrTiO_3$ (001) substrates have a twined structure, where the *a*- or *b*-axis of BSCCO is parallel to [110] $SrTiO_3$, as reported in Ref. [16]. The typical critical temperature (T_c) was 60 K for an as-grown BSCCO thin film of 100 nm thickness.

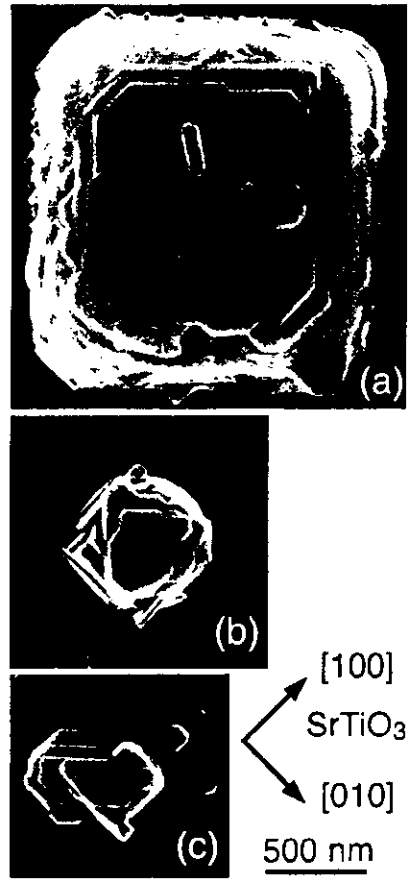

Fig. 3. SEM image of the BSCCO thin films grown on the patterned $SrTiO_3$ substrates. Areas of mesa structures are (a) 1 μm × 1 μm, (b) 0.5 μm × 0.5 μm and (c) 0.3 μm × 0.3 μm.

The chemical composition of our films was measured at an unpatterned area and was estimated to be Bi : Sr : Ca : Cu = 1.9 : 2.0 : 1.0 : 2.0.

Figure 3 shows SEM images of 70-nm-thick BSCCO thin film grown on the mesa structure with dimensions of (a) 1 μm × 1 μm × 1 μm, (b) 0.5 μm × 0.5 μm × 0.5 μm and (c) 0.3 μm × 0.3 μm × 0.1 μm. Plate-shaped crystals were observed on the top of the mesas which was made up of several facets. Plate-shaped crystals similar to those on the top of the mesas were observed on some of the side-walls. Figure 4 shows 45° oblique views of the same samples as Fig. 3. For (a) and (b), it is found that the plate-shaped crystals are grown on {001} plane of $SrTiO_3$. On the other hand, some sidewalls are free from growth of plate-shaped crystals except for some round crystals that are considered to be impurity phases consisting of the deposited elements without Bi. It is determined that BSCCO growth on the patterned structure depends strongly on the direction of the Bi beam which comes from left-hand of these images with an angle of 55°

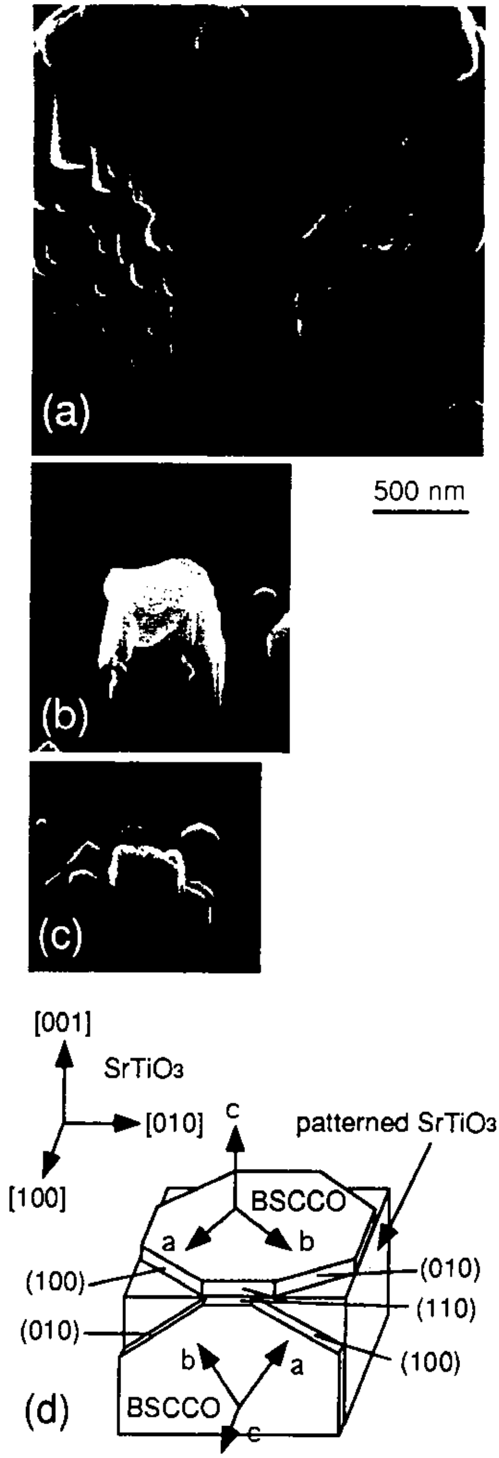

Fig. 4. 45° oblique view of mesa structure with (a) 1 μm × 1 μm and (b) 0.5 μm × 0.5 μm. (c) is a schematic drawing showing an epitaxial relationship between the BSCCO and the patterned $SrTiO_3$.

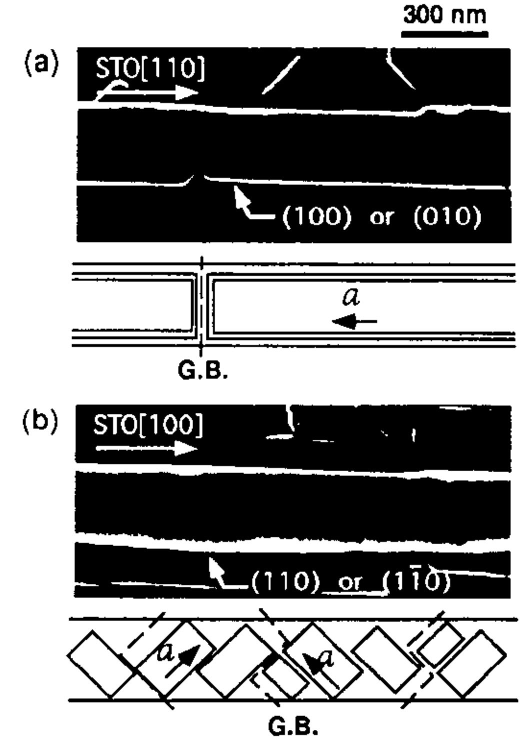

Fig. 5. SEM images of line patterns of the BSCCO thin film and schematic drawings. Lines are parallel to the [110] and [100] directions of the $SrTiO_3$ (001) substrate for (a) and (b), respectively.

to the surface. The dependence of the Bi beam has been discussed in elsewhere [17].

Considering the epitaxial relationship between BSCCO and $SrTiO_3$, it is found that the obtained structure has (100), (010), (110) and (1$\bar{1}$0) facets of BSCCO as schematically depicted in Fig. 4(d), although we could not determine which is the *a*- or the *b*-axis. (100) and (010) facets of BSCCO are formed along [110] directions of the $SrTiO_3$, and (110) and (1$\bar{1}$0) facets are along [100] directions of the $SrTiO_3$. This characteristics of facet growth has also been observed at the BSCCO thin film growth on off-axis substrates.

By utilizing the characteristics of facet growth, line patterns of BSCCO with a width of 0.3 μm and a thickness of 70 nm were fabricated. Figure 6 shows SEM images of line patterns and schematic drawings for along (a) [100] and (b) [110] directions of the $SrTiO_3$ substrate. Sharp edges were formed by (110) and (1$\bar{1}$0) facets, and by (100) and (010) for (a) and (b), respectively.

The edge of the line formed by (100) or (010) facets is straighter than those of (110) of (1$\bar{1}$0) facets. These shape has a relation to grains grown on the line patterns, which is confirmed by the SEM measurement. Rectangular 2-dimensional terraces are observed and are drawn schematically in Fig. 5. The (010) facet can grow easier than other facets except for (001) as observed at the growth on off-axis substrates. The BSCCO crystal, therefore, grows along the line along [110] $SrTiO_3$ azimuth (Fig. 5(a)), whereas it tends to grow with an angle of 45° to the line along [100] $SrTiO_3$ azimuth (Fig. 5(b)). This characteristics determines a size of the grain, and it was >1 μm and ~300 nm for (a) and (b), respectively. Furthermore, it is considered that the BSCCO line along [110] $SrTiO_3$ azimuth is a single domain structure whose a-axis aliens along [110] $SrTiO_3$ azimuth.

In the case of other etching process, such as Ar ion etching technique, although it may fabricate small structure with a micron-scale, it is impossible to fabricate in nanometer-scal. This facet growth technique utilizing the crystallographic characteristics is promising for a nano technology of the high-T_c superconductors, because it can make genuine planes and right angled corners. Furthermore, the BSCCO submicron-size structures fabricated by this technique were considered to be free from damage by various etching processes. The transport property of these submicron-size structures is under investigation.

IV. Conclusions

Submicron-size structures of BSCCO were successfully fabricated using the $SrTiO_3$ (001) substrate patterned by the FIB method. The formation of (100), (010), (110) and $(1\bar{1}0)$ facets was confirmed in the crystal grown on mesa structures with dimensions of 0.3 μm × 0.3 μm × 0.7 μm. Utilizing this crystal habit, 0.3-μm-wide line patterns of BSCCO were fabricated. This technique can be developed for the nanometer-sized fabrication of high-T_c superconductors by higher resolution patterning processes such as electron beam lithography

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