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Submicron-Size Fabrication of $Bi_2Sr_2CaCu_2O_x$ Thin Films by Utilizing Facet Growth

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Submicron-size $Bi_2Sr_2CaCu_2O_x$ (BSCCO) structures of mesa patterns with dimensions of 0.5 μm × 0.5 μm × 0.07 μm and line patterns of 0.3 μm width were fabricated on patterned $SrTiO_3$ (001) substrates. These fine structures were obtained from the growth properties of the crystal, which favor the formation of (100), (010), (110) and $(1\bar{1}0)$ facets. The c-axis oriented epitaxial BSCCO thin films were prepared by the molecular beam epitaxy (MBE) method on patterned $SrTiO_3$ (001) substrates directly written by a 30 kV Ga focused ion beam.

KEYWORDS: high-T_c superconductor, BiSrCaCuO thin film, submicron-size structure, focused ion beam, patterned substrate, molecular beam epitaxy, facet growth

1. 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. For integration and improvement of high-T_c superconducting devices, a high-resolution process 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 are few reports on facet growth for the fabrication of nanometer- or submicron-size structures.

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.[14] 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.[15] 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.

2. Experimental

The FIB apparatus SMI9200 (Seiko Instruments Ltd.) was used in this study. 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 of 0.3 – 2 μm size 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.

BSCCO thin films were prepared by a MBE method with a sequential deposition technique on 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 $\sim$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.[16,17]

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).

3. Results and Discussion

Figure 1 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. 18. The typical critical temperature (T_c) was 60 K for an as-grown BSCCO thin film of 100 nm thickness. 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 2 shows SEM images of 70-nm-thick BSCCO thin

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film grown on the mesa structure with dimensions of 0.5 μm × 0.5 μm × 0.7 μm. A *c*-axis oriented BSCCO crystal was grown on the top of the mesa. Plate-shaped crystals similar to those on the top of the mesa were observed on some of the side-walls with {001} plane of $SrTiO_3$. On the other hand, some sidewalls are free from growth of plate-shaped crystals except for some round-shaped 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. The direction of each beam during the growth is shown in Fig. 2(a). 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. 2(c), although we could not determine which is the *a*- or the *b*-axis.

In order to study the dependence of facet growth on the direction of the Bi beam, an EDX measurement was carried out on another 45°-rotated mesa pattern fabricated on the same substrate. Figure 3 shows the result of EDX area analysis: (a) is a SEM image, (b) is the configuration of beam directions and the X-ray detector for EDX measurement, and (c) and (d) are characteristic X-ray images for Ti-Lα and Bi-Mα, respectively, where the Ti image is shown as a reference. For Bi, the intensity at the part shadowed from the Bi flux is lower than those of other parts, as shown in Fig. 3(d). We investigated previously the diffusion length of adsorbed atoms during BSCCO growth by RHEED observation, and estimated it to be about 15 nm at the growth temperature of 740°C.[17] However, the difference in the diffusion length between different atomic species was not discussed. Based on the results of SEM observation and EDX measurement, it seems that the diffusion length of Bi is smaller than those of other atoms,

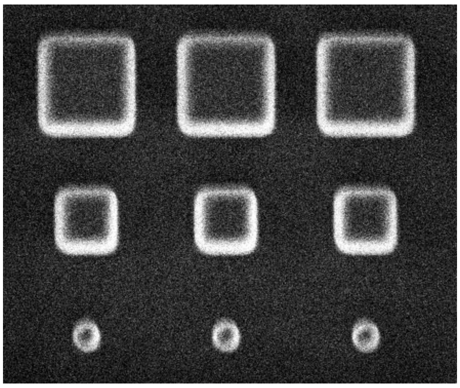

Fig. 1. SIM image of the patterned $SrTiO_3$ substrate. Areas of mesa structures are 2 μm × 2 μm, 1 μm × 1 μm and 0.5 μm × 0.5 μm and the height is 1.3 μm.

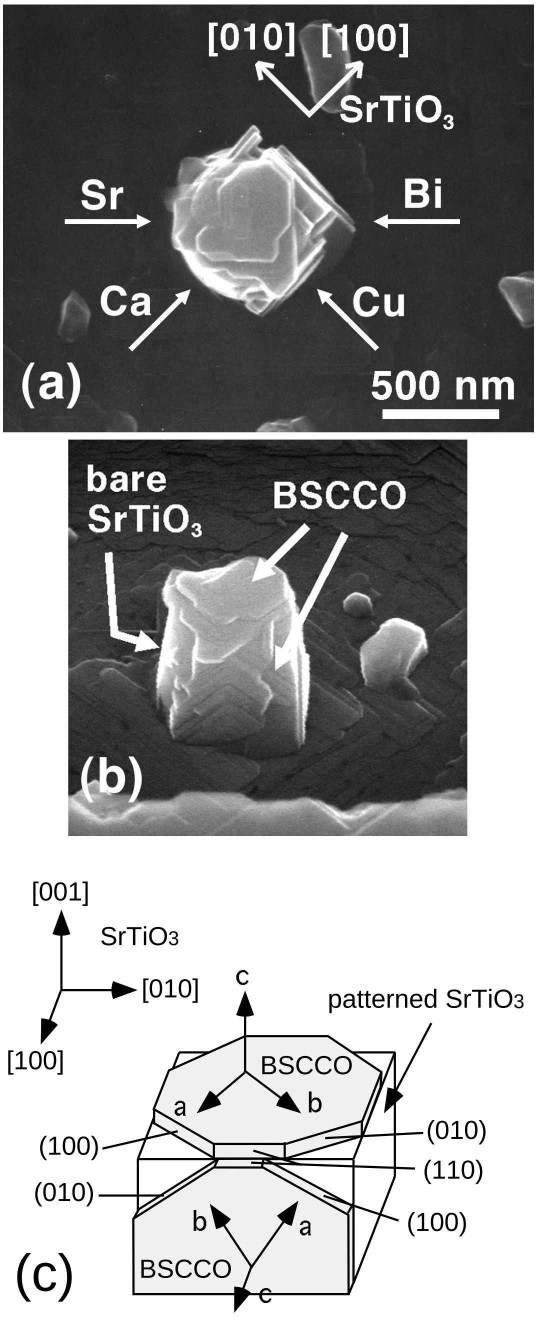

Fig. 2. SEM images of the BSCCO thin film grown on a mesa structure with dimensions of 0.5 μm × 0.5 μm × 0.7 μm : (a) Top view and (b) 45° oblique view. (c) A schematic drawing showing an epitaxial relationship. The beam direction of each element is shown in (a).

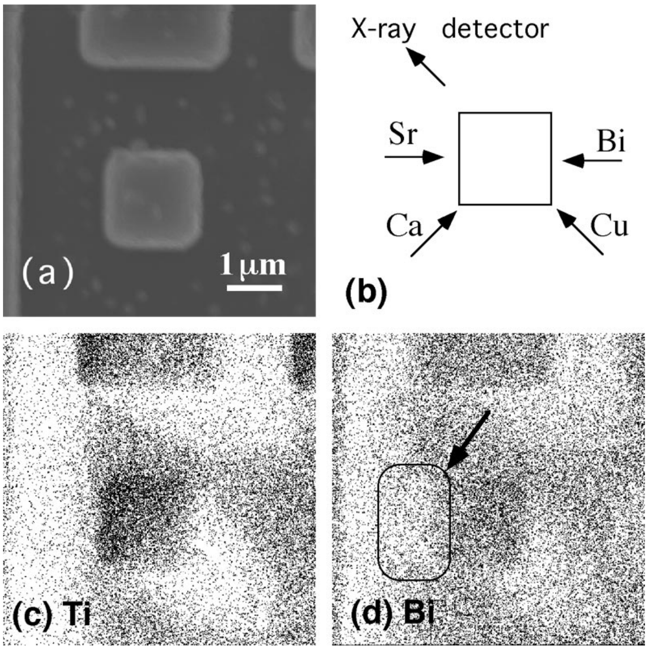

Fig. 3. (a) SEM image of BSCCO thin film grown on a mesa structure. (b) Directions of Bi, Sr, Ca and Cu beams in MBE growth, and the X-ray detector with respect to the sample. EDX mappings of (c) Ti-Lα and (d) Bi-Mα. The shadowed part exhibiting low intensity of Bi signal is enclosed by a solid line.

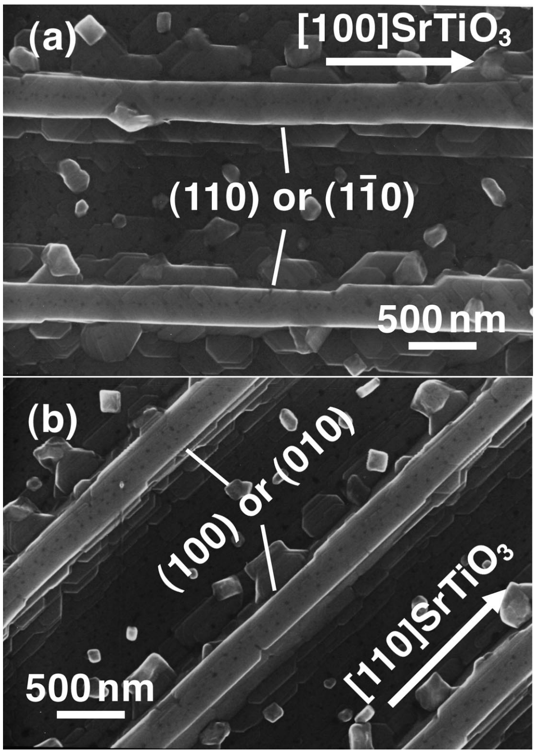

Fig. 4. SEM images of line patterns of the BSCCO thin film. Lines are parallel to the [100] and [110] directions of the $SrTiO_3$ (001) substrate for (a) and (b), respectively.

and that BSCCO thin film growth is limited by the diffusion of Bi atoms. This is consistent with the fact that Bi has a relatively high vapor pressure, so that 30% of the adsorbed Bi atoms evaporate during growth in our conditions.

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 4 shows SEM images of line patterns 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) facets for (a) and (b), respectively. These patterns are considered to be free from damage by various etching processes. The transport property of these submicron-size structures is under investigation.

4. 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 0.5 μm × 0.5 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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