Surface modification of Bi-Sr-Ca-Cu-O films deposited *in situ* by radio frequency plasma flash evaporation with a scanning tunneling microscope

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The surface modifications of as-grown superconducting Bi-Sr-Ca-Cu-O (BSCCO) films prepared by radio frequency plasma flash evaporation were carried out with a scanning tunneling microscope (STM). The as-grown films were identified as highly c-axis-oriented, low T_c (80 K) phase $Bi_2Sr_2Ca_1Cu_2O_x$ with some residue such as $(Sr,Ca)_3Cu_5O_x$ from x-ray diffraction patterns. The as-grown film deposited at about 750 °C exhibited a superconducting critical temperature T_c of 76 K and a critical current density J_c of 8.8×10^4 A/cm^2 under zero magnetic field at 27 K. The nanometer-size surface modifications between 2 and 50 nm, especially layered etching, of the prepared BSCCO films were successfully performed by using a STM in air.

Recently, nanometer-size fabrications with a scanning tunneling microscope (STM) as a powerful tool of nanotechnology[1] have been carried out intensively. While STM has been applied to nanometer-scale fabrications of various materials,[2] only surface modifications of $Ho_1Ba_2Cu_3O_x$ films were performed among many high superconducting transition temperature T_c oxides.[3] An application of this technique to Bi-Sr-Ca-Cu-O (BSCCO) films is considered to be of great interest not only for engineering but also for pure science.

In this letter, we report the results of nanometer-size surface modifications of the BSCCO films deposited *in situ* by radio frequency (rf) plasma flash evaporation with a STM in air. An rf plasma flash evaporation has been developed and applied to the deposition of $Y_1Ba_2Cu_3O_x$ (YBCO) films by our group for the first time.[4-7] In this process, mixed fine powders of the constituents are continuously injected into a rf plasma to be coevaporated completely and codeposited onto substrates under atmospheric pressure[4] or a soft-vacuum environment above about 100 Torr.[5,6] As-grown YBCO films with high T_c (>90 K) and critical current density J_c ($>10^5$ A/cm^2 under zero magnetic field at 77 K) were successfully synthesized by this method.[6] Coprecipitated $Bi_2Sr_2Ca_2Cu_3O_x$ powders of about 3 μm in size were fed into an Ar-O_2 plasma, coevaporated completely, and the composition controlled high-temperature vapors were codeposited onto (100)MgO substrates placed in a plasma tail flame. The present study is the first application to BSCCO films. The typical experimental conditions are listed in Table I. Substrates were set on a rotatable sample holder in which a chromel-almel thermocouple was attached. The duration of deposition was within 20 min and the film thicknesses were about 1 μm. After the deposition, the samples were removed from the chamber within 10 min. No extra post-annealings were carried out. The prepared films were characterized by x-ray diffraction (XRD) patterns with the Cu $K\alpha$ line, inductively coupled plasma (ICP) chemical analysis, and scanning electron micrograph (SEM). The electrical resistivity and J_c of the films were measured by a four-probe method. Nanometer-scale modification of the as-grown film after peeling off the near-surface region with Scotch tape was performed with a commercial STM (Nanoscope II, Digital Instruments Inc.) in air. The STM was used as an electron source for nanometer-size fabrication as well as a microscope for imaging by changing bias voltage (V_b) and/or duration of tunneling current (I_t) as described previously.[8] During fabrication, V_b was raised from low voltage (<1 V), used for imaging, to several volts without a feedback loop. The probe tips employed here were mechanically shaped Pt-Ir wires.

The typical XRD pattern of the film deposited at 750 °C is shown in Fig. 1, which reveals that the film mainly consisted of highly c-axis-oriented, low T_c (80 K) phase $Bi_2Sr_2Ca_1Cu_2O_x$ with some residue such as $(Sr,Ca)_3Cu_5O_x$. The average chemical compositions from ICP were Bi:Sr:Ca:Cu = 1.1:1.1:1.3:2.0. Figures 2(a) and 2(b) show the examples of SEM of the surface and cleaved cross section of as-grown film prepared at 750 °C, respectively. A dense microstructure with precipitates is observed. Figure 3 represents the temperature dependence of the dc resistivity. It is found that the superconducting critical temperature T_0 (onset) and T_c (zero resistance) are 110 and 76 K, respectively. While standard thermal plasma techniques such as spraying have been applied to prepare BSCCO films, the qualities of the as-grown films have been

TABLE I. Typical experimental conditions.

rf power	50 kW (4 MHz)
Pressure	200 Torr
Powder	$Bi_2Sr_2Ca_2Cu_3O_x$ 3 μm
Powder feeding rate	10 mg/min
Plasma gas flow rate (O_2)	40 ℓ/min
Carrier gas flow rate (Ar)	5 ℓ/min
Substrate	(100)MgO 2 mm×2 mm×10 mm
Substrate temperature	720 –770 °C

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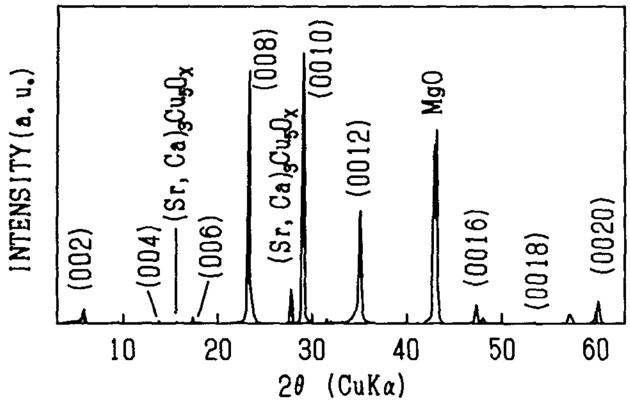

FIG. 1. XRD pattern of an as-grown Bi-Sr-Ca-Cu-O film deposited on a (100)MgO substrate.

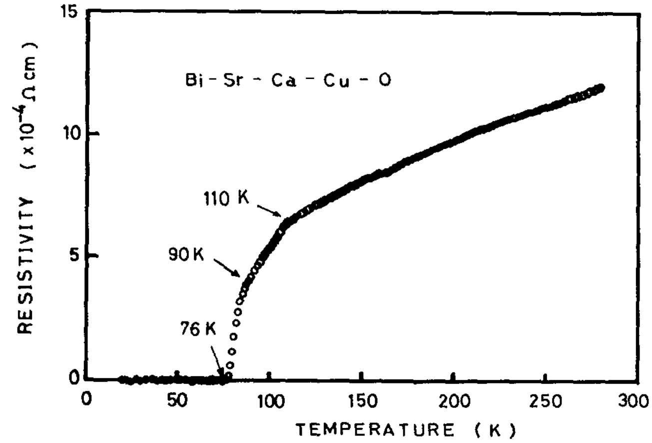

FIG. 3. Resistivity vs temperature for an as-grown Bi-Sr-Ca-Cu-O film deposited on a (100)MgO substrate.

not so good. As-grown films with T_c more than 20 K could not been prepared.[9] The drop of resistivity at 110 K suggests that high T_c (110 K) phases, $Bi_2Sr_2Ca_2Cu_3O_y$, were also partially grown in this film, while most of the film demonstrated low T_c (80 K) phases, and no clear XRD peaks of high T_c phase can be observed, as shown in XRD pattern of Fig. 1. The J_c were also deduced from the voltage-current curves by using the 10 μV/cm criterion. The value of critical current density is $J_c = 8.8\times10^4$ A/cm^2 at 27 K without magnetic field. While, at this very early stage, our results of J_c are inferior to those achieved by other methods such as sputtering ($J_c > 10^6$ A/cm^2 at 77 K),[10] this process has some advantages such as a simple procedure without any high-vacuum apparatus, high deposition rates, and adaptabilities to depositions of multicomponents systems, large-scale depositions and continuous long-time operations for practical applications, as described previously.[4–7] Further research is now in progress to improve the superconducting properties.

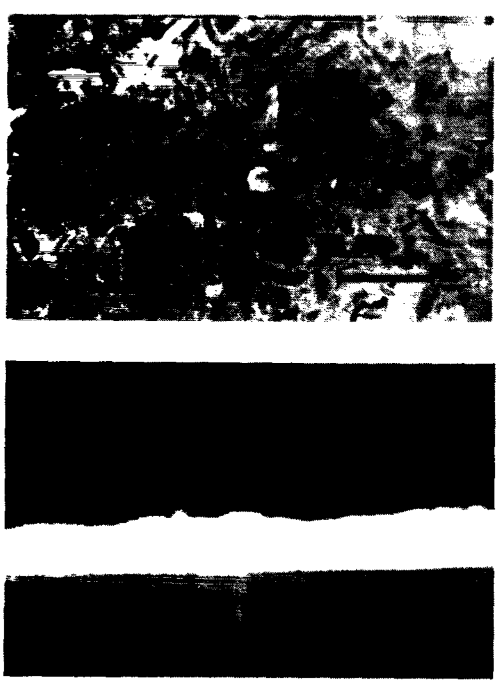

FIG. 2. Scanning electron micrographs of an as-grown Bi-Sr-Ca-Cu-O film deposited on a (100)MgO substrate: (a) surface and (b) cross section.

As mentioned above, nanometer-scale fabrications of these BSCCO films with a STM in air may be of great impact for science and technology. Nanometer structures between 2 and 50 nm can be fabricated on the surfaces with a STM in air. The examples are shown in Figs. 4(a), 4(b), 4(c), and 4(d). Figure 4(a) represents a STM image ($V_b = 0.5$ V and $I_t = 1$ nA) of a flat terrace before fabrication. Figure 4(b) shows a STM image ($V_b = 0.5$ V and $I_t = 1$ nA) of nanometer structure of about 10 nm in diameter created on the same region as shown in Fig. 4(a) by raising from $V_b = 0.5$ V with $I_t = 1$ nA for imaging to $V_b = 4.5$ V with $I_t = 1$ nA for 1 s. Interestingly, a hole with a flat bottom with depth of about 3 nm, which corresponds to c-axis lattice parameter of low T_c phase, could also be fabricated on a terrace of the film as shown in Figs. 4(c) ($V_b = 0.5$ V and $I_t = 1$ nA) and 4(d), which suggests the success of atomic-scaled layered etching. This layered lithography was performed in the case of layered materials.[11] While the mechanism of the etching is not clear, it is considered to be electron-induced chemical etching, as in the case of graphite.[12] The details will be published elsewhere.

In summary, as-grown superconducting BSCCO films were successfully prepared on (100)MgO substrates by an rf plasma flash evaporation for the first time. The XRD results indicate that the structure of the as-grown film was highly c-axis-oriented, low T_c(80 K) phase $Bi_2Sr_2Ca_1Cu_2O_x$ with some residue such as $(Sr,Ca)_3Cu_5O_x$. The as-grown film deposited at 750 °C exhibited a T_c of 76 K and a J_c of 8.8×10^4 A/cm^2 at 27 K. We succeeded in nanometer-size surface fabrications, especially, layer etchings, of the BSCCO films with a STM in air.

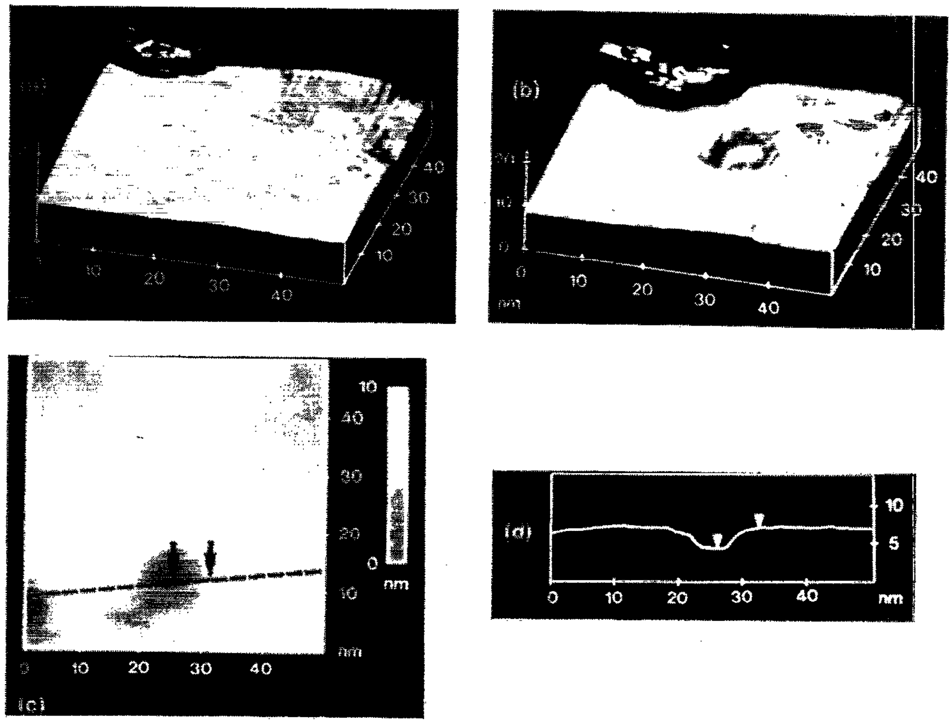

FIG. 4. Scanning tunneling micrographs taken in air: (a) surface of *c*-axis-oriented Bi-Sr-Ca-Cu-O films before surface modification, (b) nanometer structure created with a STM in air on the same region as shown in (a), (c) gray scale image of Bi-Sr-Ca-Cu-O surface layer-etched in air, and (d) the line trace of the cross section through the hole indicated in Fig. 4(c).

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