Prototyping new type Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ devices using a consumer-oriented inkjet printer

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Abstract. We have tried the microfabrication of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212) thin films. The thin films were prepared by the metal-organic decomposition method. The photoresist was printed on the thin films using a consumer-oriented inkjet printer. Filling a black cartridge with resist diluted 3 times with ethanol and printing with 80% black can minimize both the scattering of the resist and the areas where the resist is not on. After etching the thin films with citric acid, the photoresist was stripped with NaOH. Under the printing and etching conditions in this report, the resist width was about 0.05 mm wider than the desired width, and the undercut width was about 0.08 mm. We succeeded in forming a bridge of about 75 μm.

1. Introduction

Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212) has a layered perovskite structure and forms an intrinsic Josephson junction (IJJ). When a voltage is applied in the c-axis direction, an alternating current with a frequency proportional to the voltage is generated. A vibration mode excited by matching the frequency of the alternating current with a cavity resonance frequency can be used for a terahertz oscillator, which is considered to be a promising device that fills a frequency domain called the "terahertz gap". It has already been proved that a μW class continuous coherent terahertz wave can be oscillated [1-4].

The major preparation methods thus far have been reported on c-axis oriented Bi2212 that requires complicated procedures and dry etching, such as a precisely controlled etching process in depth direction in order to form the c-axis current paths. If a non-c-axis oriented thin film of which the c-axis parallel or incline to the substrate surface can be prepared, planar type IJJ devices can be fabricate simply by forming current paths parallel to the substrate [5,6]. In preparing such non-c-axis oriented thin films, it is important that selection of substrates focusing on lattice matching. If such substrates are selected and solution or powder material is coated on that substrate by a printing method, it is considered that an IJJ devices can be fabricated only by performing a heat treatment.

Our research so far has shown that crystals with c-axis parallel to the substrate can be formed by solution method [7-10]. Since we have succeeded in forming crystal grains that the c-axis is parallel to the substrate, we are now attempting on prototyping device using a consumer-oriented inkjet printer. The main component of the solvent in the Bi2212 raw material solution is xylene. Some inkjet printer components have low resistance to xylene, such as the packing of the printer head. Therefore, the Bi2212 raw material solution cannot be used by filling in the ink cartridge. In this report, microfabrication is...
performed by lithography and chemical etching. The printing method using an inkjet printer is applied to the lithography process.

2. Experimental Procedure

Bi2212 thin films under study were prepared by the metal-organic decomposition method using a stoichiometric BSCCO metal-organic solution (supplied by Kojundo Chemical Lab. Co., Ltd. SK-BSCCO008). Substrates used were SrTiO$_3$ (100) substrates with the size of $10 \times 10 \times 0.5$ mm. We are using an EPSON inkjet printer capable of CD label printing (supplied by Seiko Epson Corporation EP-777A). The photoresist ink used is Dipamat Etch Resist (supplied by AGFA Materials Japan Ltd. ER01). The samples were observed by SEM. Preparation procedures were as follows:

1. Using a spin coater, the raw material solution is applied to the entire surface of the substrate. The substrate coated with the solution is heat-treated using a box furnace in O$_2$ atmosphere. This procedure is the same as the previous report [8,10].

2. Photoresist is applied to the sample in a desired pattern using an inkjet printer.
   (A) A mount is attached to the CD/DVD tray, and the thin film sample is fixed on it with double-sided tape.
   (B) Photoresist ink is printed on the thin film sample using EPSON software “Print CD”. The ink cartridge is filled with a solution diluted with a ratio of photoresist : ethanol = 1 : 2.
   (C) The sample is irradiated with UV light for about 10 minutes using a UV lamp with a peak wavelength of 368 nm for curing photoresist.

3. Etching with acid is performed.
   (A) The film is chemically etched by immersing it in a solution of 0.5 g of citric acid in 10 ml of pure water for about 1 minute. This is performed while visually checking whether the Bi2212 films are sufficiently etched.
   (B) The sample is washed with pure water.

4. The photoresist is removed.
   (A) The photoresist is removed by immersing in 0.1 g NaOH in 20 ml pure water for about 15 seconds.
   (B) The sample is washed with pure water.

Figure 1 (a) shows the CD/DVD tray used. A mount was installed to adjust the depth of the indentation. Figure 1 (b) shows the schematic diagram (cross section) of CD/DVD tray. CD/DVD tray set up as follows: The depth of the tray recess is about 1 mm. The thickness of the pedestal is about 0.3 mm. Since the thickness of the substrate is 0.5 mm, the surface of the sample does not protrude from the tray recess.

Figure 2 shows images of the resist patterns. In normal printing, changing the color density changes the amount of ink ejected. It is considered that the amount of resist to be applied can be controlled using this fact. Therefore, the black cartridge was filled with ink diluted with ethanol, and printing was performed with the black density range of 100% (that is, RGB color code expressed in hexadecimal is #000000) to 20% (the color code is #CDCDCD). Figure 2 (a) shows the test patterns for that. The printed resist was observed with an optical microscope. The test pattern in figure 2 (b) was prepared to investigate the undercut width due to over-etching. Furthermore, it is assumed that the electrode part will have a bow-tie antenna structure for an oscillation element in the future. Figure 2 (c) shows the test pattern for that.
3. Result and Discussion

Figure 3 are images observed by an optical microscope of resist printed with the patterns of figure 2 (a) in black 100% (#000000) to 20% (#CDCDCD). In most cases, the edge of the resist was not straight, but had irregularities of several tens of μm, and the width was not uniform. Figure 4 shows the dependence of the printed resist width on the black density shown in figure 3. Each marker represents the average value of the width, and the error bar represents the variation. When the black density was 80% or more, the resist ink scattered outside the desired pattern as shown by the solid arrow in figures 3 (a) and (b). This is probably because the substrate does not absorb the solution. At 80% black, the minimum width was about 0.25 mm, the maximum was about 0.33 mm, and the average was about 0.29 mm. Since the desired resist width was 0.24 mm, the deviation from the desired value was about 0.05 mm. When black was less than 60%, as shown by the dashed arrow in figures 3 (c) - (e), there was a spot where no resist was on the inside of the desired pattern. At 20% black, there were areas where the resist was not connected almost completely. In order to etch thin films into desired shapes, it is necessary to minimize both the scattering of the resist and the areas where the resist is not applied. Therefore, when photoresist : ethanol = 1 : 2, black 80% (#343434) is considered to be closest to these desirable conditions. In the following, the discussion will be made in consideration of the fact that the width of the printed resist will be wider than the desired width of about 0.05 mm on average under these conditions.
**Figure 3.** The images observed by an optical microscope of resist printed with the patterns of figure 2 (a) in black 100% to 20%. (a) 100%. (b) 80%. (c) 60%. (d) 40%. (e) 20%.

**Figure 4.** The dependence of the printed resist width on the black density shown in figure 3. Each marker represents the average value of the width, and the error bar represents the variation.

Figure 5 shows a photograph and a SEM image of a sample prepared for testing. Portions surrounded by black broken line circles in figure 5 (b) were right-angle portion as desired patterns, but the corner was rounded. Possible reasons for these were undercuts caused by citric acid wrapping under the photoresist. Figure 6 plots the design value dependence of the actual width of the Bi2212 film after etching and that of the undercut width. The dotted line represents the average resist width under the printing conditions discussed above. The undercut width was obtained by subtracting the actual Bi2212 film width from the printed resist width. The average of the undercut width at all design values was about 0.08 mm.
Figure 5. A photograph and a SEM image of a sample prepared for testing to investigate the undercut width due to over-etching. (a) Sample photograph. (b) SEM image.

Figure 6. The design value dependence of the actual width of the Bi2212 film after etching and that of the undercut width. The dotted line represents the average resist width under the printing conditions black 80% (#343434).

Figure 7 shows a photograph and SEM image of a sample prepared for bridge formation. We succeeded in forming a bridge of about 75 μm. When the electrical connection was checked with a tester at room temperature, it was confirmed that the bridge portion was electrically connected. The portion indicated by the white dotted arrow is considered to be a region where the film thickness is thin due to undercut, and the portion indicated by the black dotted arrow is considered to be an unetched region. It is considered that the undercut region is connected at the bridge part and the film thickness at that part is thinner. The dots around the bridge are considered to be the remaining Bi2212. These dots are considered to be electrically insulated because the substrate itself is an insulator. The design value of the width of the bridge part was 0.1 mm. As mentioned above, if the width of the printed resist was about 0.15 mm and the undercut width was about 0.08 mm, it can be explained that the width was about this. In the future, we will measure the electrical characteristics and confirm whether they have superconductivity.
4. Summary
We have tried the microfabrication of Bi2212 thin films. The thin films were prepared by the metal-organic decomposition method. The photoresist was printed on the thin films using a consumer-oriented inkjet printer. After etching the thin films with citric acid, the photoresist was stripped with NaOH. As a result, the following was found.
(1) Filling a black cartridge with resist diluted 3 times with ethanol and printing with 80% black can minimize both the scattering of the resist and the areas where the resist is not on. Under these conditions, the resist width is about 0.05 mm wider than the desired width.
(2) Under the etching conditions in this report, the undercut width was about 0.08 mm. The corners were rounded. This is probably due to the undercut caused by citric acid wrapping under the resist.
(3) We succeeded in fabricating a bridge with a width of about 75 μm.

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