

Formation of As-Deposited Yb-Ba-Cu-O Superconducting Films by an Arc Discharge Evaporation Method

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A new process using DC arc discharge evaporation is presented for preparing as-deposited superconducting films of Yb-Ba-Cu-O on insulating substrates. In the arc discharge method, it is necessary to alter the applied bias direction periodically during film deposition, in order to obtain stoichiometric composition. It was found from SIMS analysis that a periodic composition change corresponding to the alternation of bias voltage existed in the film and this layered structure did not diffuse out even after annealing at 800°C for 2h. Based on these results, the alternation period was shortened and the deposited layer thickness per cycle was decreased to 1nm, which was close to a monolayer. The resultant film deposited on SrTiO₃(100) at 700°C showed zero resistivity at 62K without any further heat treatment.

1. INTRODUCTION

With the discovery of superconductivity above 90K (Ln-Ba-Cu-O:Ln=rare earth; Y, Yb, Er, Ho, etc.)¹⁾ has come extensive research on thin films. Recently, importance of as-deposited superconducting films has been increasing. So far, several deposition methods, including sputtering²⁾, molecular beam epitaxy³⁾, vacuum evaporation (electron beam or resistive heating evaporation)⁴⁾, and laser ablation⁵⁾, have been reported. Previously we reported a new method of preparing Yb-Ba-Cu-O superconducting films, in which DC arc discharge evaporation from bulk ceramic sources is used.⁶⁾ Superconductive and related ceramics show metallic or semiconductive properties in electrical conductivity near or above room temperature. Thus, they can be used as electrodes through which current for joule heating flows and arc discharge due to thermionic electrons can be expected. In this paper we present that as-deposited superconducting films have been grown on SrTiO₃(100) at substrate temperature of 700°C by an arc discharge evaporation.

2. EXPERIMENTS

The apparatus for the DC arc discharge evaporation method is shown in Fig. 1. It is a vacuum evaporation system with a base pressure of about 1×10^{-5} Pa, in which an ordinary electron beam gun or a resistive heater is replaced by an arc discharge source. The vacuum pressure during film deposition was kept around 1.3~2.6 Pa by introducing O₂ gas in the chamber, so that the arc discharge was stabilized and oxygen atoms were incorporated in the deposited films. The electrode for arc discharge was made of Yb-metal. On the other hand, evaporation sources were made of Y_XBa_YCu₃O_Z (X=1~2.5, Y=2~2.5) ceramics. They had been fabricated from Ln₂O₃, Ba(NO₃)₂, and CuO powders by mixing, calcining, reducing them into powder, 2nd calcining, pressing the calcined powders into pellets ($\phi=15\text{mm}$; $t=5\text{mm}$), and sintering them. The substrates used for film deposition were SrTiO₃(100), MgO(100), and Al₂O₃(1 $\bar{1}$ 02). They were heated at temperature ranging from R.T. to 700°C during the deposition. The discharge was performed under a DC constant current of 1~2 A, while the applied voltage between the electrode and source

was changed from 10 to 80 V. We used a DC power supply in which the output polarity was changed and the current was independently adjusted for each polarity.

Finally, the crystalline quality of the films was characterized by X-ray diffraction analysis and Rutherford Backscattering Spectroscopy (RBS), and their composition ratio was examined by RBS and Electron Probe Microanalysis (EPMA). The measurement error between RBS and EPMA was the order of 10%. The depth profile was measured by Secondary Ion Mass Spectrometer (SIMS). The temperature dependence of the electrical resistivity was also measured for the annealed samples using a DC four-point probe method.

3. RESULTS AND DISCUSSION

It was found from the preliminary experiments that the film composition depended strongly on such parameters as the source composition, metal electrode materials, and polarity of the applied DC voltage, and that the fraction of Yb in the film was much larger in the case when the positive voltage was applied to the Yb metal electrode (the forward bias) than in the case of the backward bias. On the other hand, the Ba fraction was smaller under the forward bias condition.

We conclude from these results that a combination of the Yb electrode and Y-Ba-Cu-O sources with nonstoichiometric composition is most promising for preparation of stoichiometric Yb-Ba-Cu-O films and that alternation of the applied voltage direction is also necessary during arc discharge. In order to adjust the composition ratio precisely, the alternation was done in every preset count in the thickness monitor.

Figure 2 shows the normalized composition ratios ($3Yb/Cu$ and $3Ba/2Cu$) plotted as a function of $t_F/(t_F+t_B)$, where t_F is the layer thickness which was deposited under the forward bias and t_B is the layer thickness which was deposited under the backward bias. In this

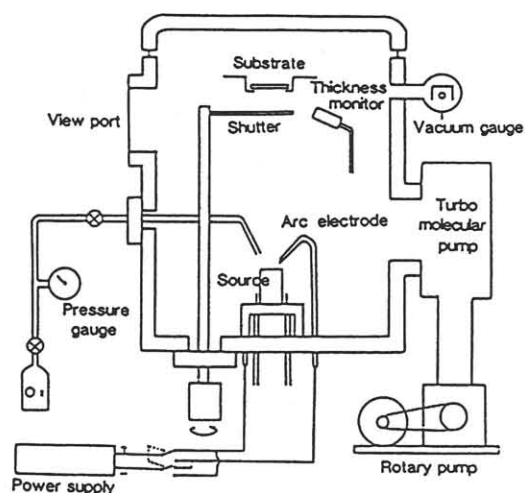


Fig. 1. Schematic drawing of an arc discharge evaporation system.

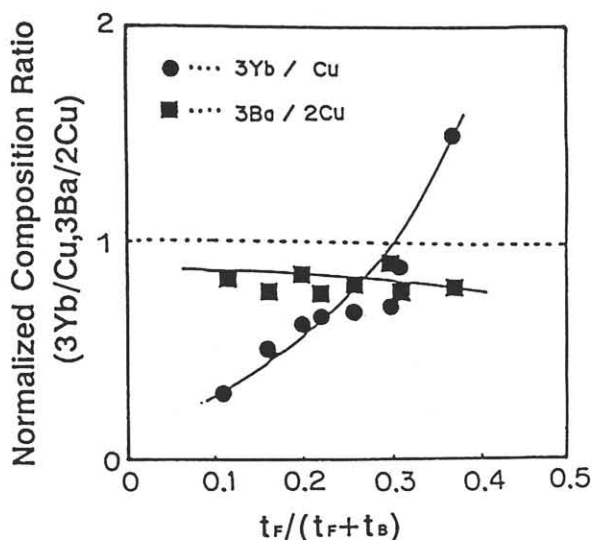


Fig. 2. Normalized composition ratio ($3Yb/Cu$ and $3Ba/2Cu$) plotted as a function of $t_F/(t_F+t_B)$.

experiment, the polarity of the applied voltage was changed in every preset thickness, and it was measured by thickness monitor. The composition ratio in the films was measured by RBS and EPMA, which revealed that the Y fraction was negligibly small under these conditions. In the normalized composition in the figure, the stoichiometric value is unity for both Yb and Ba. We can see from this figure that the Yb fraction is increased with increase of the forward bias duration, while

the Ba fraction is decreased with it. We can also see that in order to satisfy the stoichiometric condition in the film, it is necessary to use an $Y_{2.3}Ba_{2.1}Cu_3O_z$ source and to choose the fraction around 0.30 in the horizontal axis.

Based on the results in Fig. 2, arc discharge sources with the optimum composition ratio were prepared and films were deposited at room temperature using the alternative bias condition which satisfies the stoichiometric film composition. The film thickness is $2.0\mu m$ with 30nm/cycle. The as-deposited films were amorphous and they were insulators in electrical properties. The films were then annealed at $930^\circ C$ for 2 hours in O_2 atmosphere. The maximum annealing temperature was After annealing, the film surfaces became rough and the films on MgO substrates showed superconductivity. A typical result on the temperature dependence of the resistivity is shown in Fig. 3, in which drastic decrease of the resistivity begins at $T_{con}=83K$ and the zero resistivity is realized at $T_{cend}=81K$. X-ray diffraction patterns of the same sample showed strong preferential orientation of the c-axis perpendicular to the substrate.

It is desirable to grow superconducting films at low temperature in order to apply it to electronic devices. So, we tried to heat the substrate during deposition. The substrate temperature was changed from room temperature (RT) to $750^\circ C$. However, no as-deposited films showed superconductivity in the temperature range down to 30K, although they showed good superconductivity after annealing at $930^\circ C$ for 2 hours in O_2 atmosphere.

In order to clarify the reason why the as-deposited films did not show superconductivity, the depth profiles of each element were measured by SIMS in both RT-deposited and annealed samples. 10keV Cs^+ ions were used as primary ions and negative ions were detected as secondary ions. In this experiment, Yb-Ba-Cu-O films were deposited on $Al_2O_3(1\bar{1}02)$ sub-

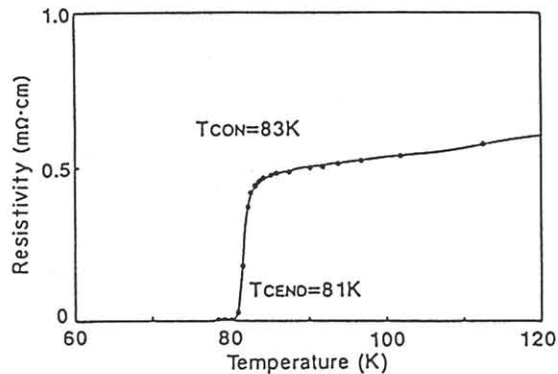


Fig. 3. Temperature dependence of resistivity of an Yb-Ba-Cu-O film. ($T_{sub}=R.T.$, $930^\circ C$ annealed)

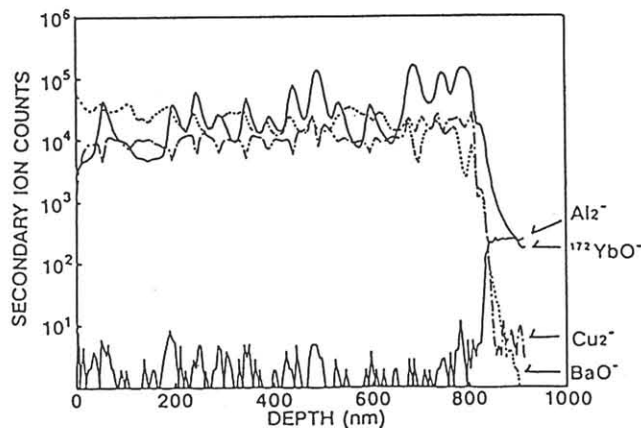


Fig. 4. SIMS analyses of an as-deposited Yb-Ba-Cu-O film on sapphire. ($T_{sub}=R.T.$)

strates. The film thickness is $2.0\mu m$ with 60nm/cycle. A typical result for a RT-deposited film is shown in Fig. 4. We can see that the YbO^- intensity changes oscillatorily, which corresponds to the alternation period of bias directions. As expected, thickness of each layer was about 60nm. It was also found that decrease of the oscillation amplitude due to diffusion of elements did not occur significantly even after annealing at $800^\circ C$. We conclude from these results that the thickness of each layer should be decreased at least by a factor 10 in order to obtain as-deposited superconducting films at temperatures less than $700^\circ C$.

The above condition was satisfied by

shortening the duration of each bias direction and by setting the MgO(100) and SrTiO₃(100) substrates farther from the source. Under the improved conditions, the film thickness was 0.1 μ m and the deposited layer thickness per cycle was about 1nm. Fig. 5 shows ρ -T curves of Yb-Ba-Cu-O films deposited in this way at 650°C and 700°C. We can see that the film deposited at 650°C didn't show zero resistivity in the temperature range down to 30K, and that the film deposited at 700°C showed zero resistivity at 57K on MgO(100) and at 62K on SrTiO₃(100). From these results, we speculate that the deposition temperature is further decreased by decreasing the deposition rate and by adjusting the composition ratio more precisely.

4. CONCLUSION

Superconducting Yb-Ba-Cu-O films were successfully prepared using an arc discharge evaporation method. After annealing at 930°C for 2 hours in O₂ atmosphere, the films on MgO(100) showed superconductivity at T_{cend}=81K. It was found from SIMS analysis that the alternation period of the applied voltage was too long and pronounced intermixing did not occur even after annealing at 800°C. Based on there results, the alternation period was shortened and the deposited layer thickness per cycle was decreased to 1nm, which was close to a mono layer. The resultant film deposited on SrTiO₃(100) at 700°C showed zero resistivity at 62K without any further heat treatment.

This method is considered to be useful to grow Yb-Ba-Cu-O films epitaxially on single crystalline insulator/Si structures.

ACKNOWLEDGMENTS

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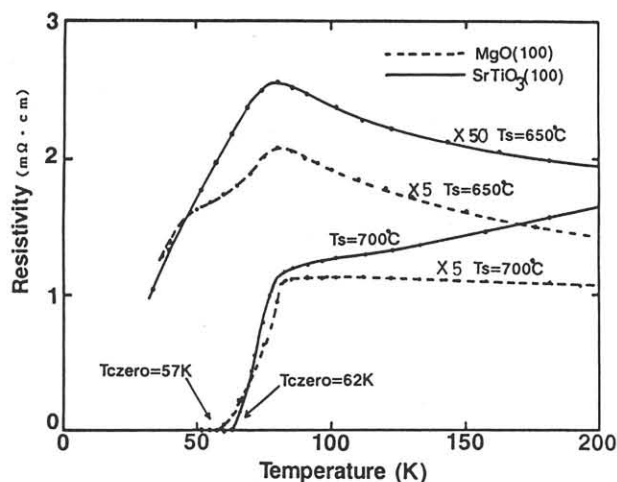


Fig. 5. Temperature dependence of resistivity of an as-deposited Yb-Ba-Cu-O film. (T_{sub}=650°C/700°C)

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