Evaluation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ /metal Ag composite thick film

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Abstract

High T_c superconductor/metal Ag composite thick film has been fabricated on PSZ substrate. By controlling the fabrication conditions, the critical current density at 77 K was elevated to 1300 A/cm^2 . The c-axis of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ plate in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ /metal Ag composite thick film was preferably oriented perpendicular to the substrate, though the non-conducting phases of $\text{Ba}_1\text{Cu}_1\text{O}_2$, $\text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5$ etc were 40 % in volume.

Key words : High T_c superconductor, superconductor/Ag metal composite, superconductor thick film

1.Introduction

It has passed about 3 years after Bednorz and Muller discovered the high T_c superconductor.1) Extensive investigations for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ have been initiated toward ceramics and thin film. However, thick film using a superconductor is very important for electronic applications. In general, the thick film technology represented by a thick film resistor has been achieved by the existence of glass. However, this technology cannot be applied to prepare the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ thick film, because of reaction between $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and glass. In previous paper, we had reported that Ag_2O addition to $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ thick film enhanced the superconducting property.2,3) Moreover, we obtained high critical current, 1300 A/cm^2 , at 77K by controlling the fabrication conditions.4,5) In this paper, we will discuss the mechanism of high current density in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ /metal Ag thick film.

2.Experimental procedure

Preparations of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ powder and mixed paste of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and Ag_2O were described in detail in references 2,3. These mixed paste were screen-printed on PSZ substrate. After drying, these thick films were sintered at the temperatures from 910 to 985 C for 3 min in O_2 atmosphere. The resistivity change measured by four probe method at 300 to 77 K. The current for measurement of resistivity was 1 mA and cooling rate around transition point to superconducting state was 0.5 C/min. The critical current density was calculated by the measured current where the output voltage was occurred by $1 \mu \text{ V/cm}$.

3.Experimental results and discussions

Figure 1 shows the resistivity vs temperature of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ thick film on Al_2O_3 ceramics substrate. The $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ /glass thick film shown in mark (1) in this figure was made by the mixture of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and glass. The resistivity was increased as same as the behaviour of semiconductor with decreasing the temperature. Similarly, the resistivity - temperature relationship from $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ thick film on Al_2O_3 ceramics substrate was shown by mark (2) in figure. Below 80 K, the resistivity was decreased and became to zero at 25 K. The one part of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ reacted to the Al_2O_3 substrate. As described in these two examples, the Al_2O_3 ceramics can not use as a substrate. Figure 2 shows the resistivity-temperature relationship of the specimens with various contents of Ag_2O (0,10,30 wt% as the content of Ag_2O , after sintering Ag_2O changed to

Fig.1 Changes of resistivity in $Y_1Ba_2Cu_3O_{7-x}$ /glass and $Y_1Ba_2Cu_3O_{7-x}$ thick film on Al_2O_3 ceramics substrate

Fig.2 Changes of resistivity in $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag with various Ag_2O contents

metal Ag) on partially stabilized ZrO_2 substrate (PSZ). The resistivity of $Y_1Ba_2Cu_3O_{7-x}$ thick film without metal Ag on PSZ substrate exhibits almost constant value in the normal conduction region and the transition to superconducting state yields sharply. The transition temperature was 80 K. On the other hand, in addition of Ag_2O , the resistivity change in the normal conduction region become metallic and the transition temperature elevated to 85 K ($Ag_2O=10$ wt%) and 90 K ($Ag_2O=30$ wt%). The critical current density at 77k was $1300 A/cm^2$ as the highest value, where the film thickness and width were $28 \mu m$ and $5.0mm$, respectively and the input current was 1.84 A. Figure 3 illustrates the output voltage vs current density sintered by 910 C (shown by mark (a) in Fig. 3, similar to following), 950 C (b), 980 C (c) and 985 C (d), respectively for 3 min in O_2 atmosphere. Figure 4 shows the typical microstructure of cross section in $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag thick film. Plate like crystalline shown by arrow a was $Y_1Ba_2Cu_3O_{7-x}$ and the c-axis was preferably oriented perpendicular to the PSZ substrate. The size of plate was about $30 \mu m$. There are other phases shown arrows b and c. The chemical compositions by EDX were $BaCu_2O_3+Y_2O_3$ and $BaCuO_2+Y_2O_3$, respectively. In general, the $BaCuO_2$ phase exhibits the liquid like block shown in arrow c. We could observed the almost same figure in $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag thick film with high critical current density. For study the reaction process between $Y_1Ba_2Cu_3O_{7-x}$ and Ag_2O , Figure 5 shows the schematic configuration, where metal Ag with a spherical shape put on the $Y_1Ba_2Cu_3O_{7-x}$ sintered block and heat-treated by the temperature of 935, 945 and 950 C, respectively for 1hr. Behaviors of metal Ag were schematically illustrated in Fig.5. Firstly, at 935 C, the color in the surface of $Y_1Ba_2Cu_3O_{7-x}$ attached to metal Ag changed from black to green. This phase was determined as $Y_2Ba_1Cu_1O_5$ by EDX. Secondly, metal Ag was half-melt and sank in the $Y_1Ba_2Cu_3O_{7-x}$ block at 945 C and above 950 C, metal Ag was penetrated into $Y_1Ba_2Cu_3O_{7-x}$ block,

Fig. 3 Critical current density of $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag composite thick film on PSZ substrate prepared by various fabrication conditions

Fig. 4 SEM micrograph of $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag composite thick film on PSZ substrate

though the shape of $Y_1Ba_2Cu_3O_{7-x}$ block was not broken. Figure 6 shows the SEM micrographs at the interface between $Y_1Ba_2Cu_3O_{7-x}$ and Ag in the configuration of Fig. 5(a) and (c). Needle shape crystallines can be observed in Fig. 6(a). Therefore, it could be confirmed that the $Y_1Ba_2Cu_3O_{7-x}$ phase attached to metal Ag transformed to $Y_2Ba_1Cu_1O_5$ phase by following chemical Eq.(1),

On the other hand, the surface attached to metal Ag heat-treated above 950 C changed to liquid like surface as same as that shown by arrow b in Fig. 4. These structures can frequently observed in $Ba_1Cu_1O_2$ phase. By the chemical analysis using EDX, these detected phases were $Ba_1Cu_1O_2$ including Y_2O_3 ($Y_1Ba_2Cu_2O_x$, $Y_1Ba_3Cu_3O_x$, $Y_1Ba_4Cu_4O_x$ and $Y_1Ba_{10}Cu_{10}O_x$) and almost same phases were observed in $Y_1Ba_2Cu_3O_{7-x}$ /Ag metal thick film. Figure 7 shows the X-ray diffraction patterns of $Y_{0.5}Ba_1Cu_1O_x$ heat-treated by the temperatures of 920, 940 and 960 C, respectively for 1 hr. The $Y_1Ba_2Cu_3O_{7-x}$ phase can be seen in each heat-treatment. On the other hand, the phase detected around $2\theta = 30$ deg became clear with increasing the heat-treated temperature. In general, these phases around $2\theta = 30$ deg were $Ba_1Cu_1O_2$ and $Y_2Ba_1Cu_1O_5$. However, X-ray peaks of $Ba_1Cu_1O_2$ and $Y_2Ba_1Cu_1O_5$ were overlapped in each other and it was very difficult to distinguish from either $Ba_1Cu_1O_2$ or $Y_2Ba_1Cu_1O_5$ when the $Ba_1Cu_1O_2$ and $Y_2Ba_1Cu_1O_5$ were coexisted. However, we has confirmed $Y_2Ba_1Cu_1O_5$ phase in $Ba_1Cu_1O_2$ phase and the coexistence of $Y_1Ba_2Cu_3O_{7-x}$ and $Ba_1Cu_1O_2$ phases by TEM. From these results, a high critical current density in the $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag thick film can be related as following.

- (1) The improvement of film density in the $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag thick film with increasing the film density, the critical current density was increased from 1 A/cm² to 1300 A/cm² because of decreasing the necks between grain to grain, where the current flow were restricted.
- (2) The grain orientation of $Y_1Ba_2Cu_3O_{7-x}$ phase
In general, the current in $Y_1Ba_2Cu_3O_{7-x}$ flow in the a-b planes (Cu planes)

Fig.5. Schematic configuration of interface between metal Ag and $Y_1Ba_2Cu_3O_{7-x}$ sintered block heat-treated by various temperature

Fig.6. SEM micrographs at the interface between metal Ag and $Y_1Ba_2Cu_3O_{7-x}$ sintered block

Therefore, if the c-axis was oriented normal to the substrate, we can expect the high current density.

(3) The existence of $Ba_1Cu_1O_2$ phase

Many efforts has been attempted how the non-superconducting phases could be decreased. On the other hand, as far as the substrate utilized in thick film, some kinds of reaction at the interface between film and substrate occurred. In the $Y_1Ba_2Cu_3O_{7-x}$ /metal Ag thick film, the chemical reaction yielded as follows,

The $Ba_1Cu_1O_2$ phase play as the liquid phase and densification of $Y_1Ba_2Cu_3O_{7-x}$ was improved.

Fig.7. X-ray diffraction patterns of $Y_{0.5}Ba_1Cu_1O_x$ heat-treated by temperatures of 960, 940, 920 C, respectively in Fig.(a),(b) and (c)

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