

High Temperature Superconductor Thick Films on Alumina Substrates

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The objective of this study is to utilize the recently discovered superconductor at temperatures above 90K¹ and to develop an optimum thick film depositing technique (2, 3) for application to high-frequency electronic devices, hybrid circuits, sensors, and electromagnetic shielding. This requires an easy method of depositing films on substrates, a reasonable value of critical current density at liquid nitrogen temperature, and excellent adhesion to the substrates being used. We have chosen the polycrystalline Al₂O₃ as substrate material because it is relatively inexpensive and can be manufactured to various shapes very easily. In order to minimize the resistivity at room temperature, we have mixed Ag₂O powder with the 123 compound. Because the melting point of Ag is 961°C, Ag₂O decomposes into Ag and form a composite (4, 5).

In order to find an optimum fabrication method on ceramic substrates, there is a broad range of parameters, such as the percentage of mixed Ag₂O, the temperature and timing of heat-treatment, and thickness of films, all of which must be varied in order to obtain higher critical current density and lower room temperature resistance of the films. In this technical note, we report the exploration of some parameter combinations and show the corresponding electrical measurements. The thick films deposited on alumina substrates have low resistivity at room temperature (films with Ag₂O), reasonable critical current density, and excellent adhesion to substrates (6, 7). Samples have been reproduced successfully and representative results are reported.

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All of the samples discussed in this paper are processed in an oxygen flowing quartz tube. The samples are sintered at appropriate temperatures and are then slowly cooled to 450°C (at the rate approximately 100°C/h) before being removed from the furnace. The critical current density (J_c) has been measured at 77 K as what was described in Ref. (8).

Our results of YBa₂Cu₃O_{7-x} thick films sintered at 950°C for 6h have shown that the critical current density is very low and adhesion to the substrates is poor. The films with 5% silver oxide sintered at 950°C have higher critical current density and have much improved adhesion to the substrates. We found that the critical current density increases nonlinearly as the film thickness increases.

To further increase the critical current density, we try to fuse the superconducting particles together and increase film density by increasing the temperature for heating. Our preliminary exploration of higher temperature heat-treatment is summarized in Table I. The samples without Ag₂O have YBa₂Cu₃O_{7-x} only, which is called recipe 1. The powder used for recipe 2 consists of 5% Ag₂O powder and 95% YBa₂Cu₃O_{7-x} powder. Samples B, D, H, I, and J have all been fabricated using the powder described in recipe 2. Sample K also contains 5% Ag₂O, but we directly mixed Ag₂O powder with Y₂O₃, CuO, and BaCO₃ powder, sintered this mixture at 920°C for 12h and then ground it into powder. We refer to this powder as recipe 3. Sample L is prepared in a similar manner to sample K except sample L has 20% Ag₂O which is referred to as recipe 4. These powders were mixed with printing vehicle to form pastes which were then screen printed or directly painted on ce-

Table I. Sample identification, paste recipes, heat-treatments and summary of electrical measurements

Sample	Mixed with Ag ₂ O	Heat-treatment in an O ₂ ambient	Thickness (μm)	Critical current density (mA/cm ²)	T _c onset (K)	T _c completion (K)	Resistivity at room temperature (Ω · cm)
A	No	Heated at 1040°C for 10 min, slowly cooled to 910°C and sintered at 910°C for 12h	150	3.68 × 10 ³	90	78	2.63 × 10 ⁻³
B	Yes	Same as above	100	156	92	79	1.5 × 10 ⁻⁴
C	No	Heated at 1050°C for 10 min, slowly cooled to 450°C	30	3.78	95	82	1.12 × 10 ⁻²
D	Yes	Same as above	30	23.9	84	78	3.34 × 10 ⁻³
E	No	Heated at 1040°C for 10 min, slowly cooled to 450°C	600	5.8 × 10 ³	98	81	3.09 × 10 ⁻³
F	No	Same as above	50	7.6 × 10 ³	89	78	3.06 × 10 ⁻³
G	No	Same as above	150	1.24 × 10 ⁴	98	82	3.81 × 10 ⁻³
H	Yes	Same as above	100	3	84	78	3 × 10 ⁻³
I	Yes	Same as above	600	1.04 × 10 ³	92	79	5.93 × 10 ⁻⁴
J	Yes	Same as above	800	3.81 × 10 ³	100	82	6.0 × 10 ⁻⁴
K	Yes	Same as above	150	1.38 × 10 ⁴	98	81	4.2 × 10 ⁻⁴
L	Yes	Same as above	150	1.67 × 10 ⁴	96	81	2.75 × 10 ⁻⁴

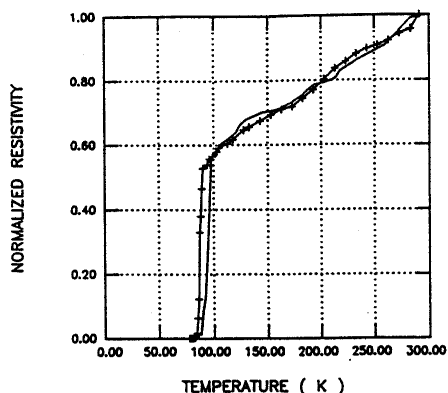


Fig. 1. Normalized resistivity (normalized to room temperature) vs. temperature for sample F (curve with +) and sample K (curve without symbol).

ramic substrates. All of the samples are fire treated in the quartz annealing tube at a temperature of 520°C for half an hour to remove printing vehicle. Samples A and B are loaded into an oven preheated to 1040°C for 10 min, then slowly cooled to 910°C and sintered at 910°C for 12h. Samples C and D are loaded into an oven preheated to 1050°C for 10 min and then slowly cooled to 450°C. Similarly, samples E-L are loaded into an oven preheated to 1040°C for 10 min and then slowly cooled to 450°C.

Comparing sample A with Sample E, F, and G shows that a shorter sintering time (without 910°C sintering) can increase the critical current density. Note that sample F has only a thickness of 50 μm and still has a reasonably high critical current density. This may be caused by increased impurities from substrates and the subsequent microstructure changes during long sintering time. Samples C and F had the same thickness before undergoing heat-treatment. The heat-treatment at 1050°C increased the density of sample C but lowered the conductivity at room temperature and the critical current density significantly. Only thick films (600 μm or thicker) by recipe 2 can have high critical current density. The critical current density of samples K and L (by recipes 3 and 4, respectively) is considerably higher than that of samples I and J (recipe 2), and samples K and L are much thinner than samples I and J. From Table I, note that the room temperature resistivity of films with Ag₂O is lower than that of films without Ag₂O. We believe that silver plays a dominant role in reducing the room temperature resistivity (5) by fusing the superconductor grains together to form a better conducting path.

As can be seen in Table I, thicker films demonstrate higher T_c . Typical resistivity vs. temperature curves for

samples F (50 μm thickness) and K (150 μm thickness) are shown in Fig. 1. The resistivity of sample F continuously decreases as temperature decreases, which is in contrast to what was observed in Ref. (6, 9).

All of the films sintered at 1040°C or higher demonstrate excellent adhesion to the substrates. This has been tested by scratching the films with a diamond scribe and breaking the films coated on substrates. These two methods could not separate the films from their respective substrates.

The thick films have shown adverse reactions with water vapor (10). As a typical case, sample E has been cooled to 77 K where the measured critical current density was 5.8 A/cm². The sample was then exposed to air and warmed to room temperature (the thick film color changed from black to gray). The sample is then cooled to 77 K again where the critical current density is now measured to be 22 mA/cm². From these results we conclude that the storage and operation of the thick films must be in an extremely dry environment.

The results of this study have shown that the critical current density depends on the thickness of the films on the ceramic substrates and can be enhanced by adding Ag₂O. The room temperature resistivity can also be decreased by adding Ag₂O to the films. Reproducible critical current density and room temperature resistivity have been achieved for samples presented in this paper. We would like to thank Professor M. K. Wu for his suggestion to add Ag₂O in thick films.

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