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Thick films of fluorine-doped $YBa_2Cu_3O_y$ were screen printed on highly polished alumina, magnesia spinel, strontium titanate, and yttria-stabilized zirconia (YSZ) substrates. They were annealed at 1000 ^oC and soaked in oxygen at 450 ^oC followed by slow cooling to room temperature. The films were characterized by electrical resistivity measurements as a function of temperature and by x-ray diffraction. The film on YSZ showed the best characteristics with a T_c(onset) of 91 K, T_c(R=0) of 88.2 K, and a transition width, ΔT_c(10-90%), of ~1.7 K. The film adhesion, probably controlled by interdiffusion of cations between the film and the substrate, was good in all cases except on strontium titanate where the film completely detached from the substrate.

INTRODUCTION

Deposition of high quality superconducting oxide films is of crucial importance both from fundamental as well as technological viewpoints. High T_c superconducting films may find applications in various high speed microelectronic devices and microwave electronic circuits. Screen printing is a simple and straightforward technique for deposition of thick films. Using this method, electronic and microwave circuit patterns and devices can be directly printed on the substrates, thus circumventing the etching and photolithographic steps. This is of particular importance for films of $YBa_2Cu_3O_{7-x}$ superconductor because of its high reactivity[1] with moisture and other chemicals.

In an earlier study[2] it was reported that the superconducting transition temperature (T_c) of bulk $YBa_2Cu_3O_{7-x}$ is both increased and sharpened on doping with low concentrations of fluorine. The composition $YBa_2Cu_3F_{0.066}O_y$ was shown to have the highest T_c and the sharpest transition width, i.e. ΔT_c (10-90%) of 0.7 ± 0.1 K. It was, therefore, interesting to see if the thick films of this composition would show any improvement in superconducting properties over the undoped films. Superconducting thin films of fluorine-doped Y-Ba-Cu-O have been produced[3] on yttria-stabilized zirconia substrates from metal trifluoroacetate spin-on precursors. These films exhibited sharp resistive transitions with zero resistance at ~92-94 K and 10-90% transition width of 1.5-1.7 K.

The objectives of the present study were the preparation of thick films of fluorine-doped Y-Ba-Cu-O superconductor by screen printing on several ceramic substrates and the investigation of the influence of fluorine doping and substrate material on the superconducting characteristics of the films.

EXPERIMENTAL

Fluorine doped superconducting powder of stoichiometric composition $YBa_2Cu_3F_{0.066}O_y$ was synthesized from Y_2O_3 (Molycorp 99.99%), $BaCO_3$ (ALFA technical grade), CuO (ALFA ACS grade), and YF_3 (REaction 99.99%) powders by a solid state reaction procedure[2]. Fine (-500 mesh) powder was mixed with an appropriate amount of 1-heptanol (Aldrich) resulting in a thick paste which was printed on various flat ceramic substrates through a 325 mesh stainless steel or silk screen. The substrate materials used were high-purity alumina (superstrate 996 from Materials Research Corporation), 9.5 mol% yttria stabilized cubic zirconia (YSZ) from CERES, magnesia (S-145 spinel) and strontium titanate both supplied by Transtech, Inc. The films were dried at ~300 ^{o}C for ~ 2 h in an oven. They were then heated at 5 ^{o}C/min to 1000 ^{o}C, sintered for 5 or 15 minutes, cooled at ~3 ^{o}C/min to 450 ^{o}C, annealed for 3 h, and then finally slow cooled to room temperature. The entire sintering and annealing cycle was carried out in flowing oxygen. The film thickness was ~30 - 60 μm as determined using a surface profile measuring system (Dektak IID, Sloan Technology Corporation).

No chemical analysis for fluorine was carried out in the sintered films. However, it may be pointed out that in our earlier work[2] on fluorine doped $YBa_2Cu_3O_{7-x}$ bulk HTS, no loss of fluorine was observed after sintering. The phases present in the films were identified from x-ray diffraction patterns which were recorded at room temperature in the 2θ range 10 - 80^o using a step scan procedure (0.03^o/2θ step, count time 0.4s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing copper K_α radiation. Electrical resistivity and its temperature dependence were measured in the standard four-probe configuration. Silver paint was used to attach the leads.

RESULTS AND DISCUSSION

We had recently reported[4,5] that the optimum sintering temperature for $YBa_2Cu_3O_{7-x}$ screen printed films on alumina is 1000 ^oC. In the present study, the films on several ceramic substrates were, therefore, baked at this temperature for 5 or 15 minutes. Physical appearance and the adhesion between the HTS film and various ceramic substrates are listed in Table I. All films were black in color and showed good adhesion except the one on $SrTiO_3$ which had completely detached from the substrate. This is quite surprising as the thermal expansion mismatch between the HTS and $SrTiO_3$ is much less than in the case of the alumina substrate as seen from the thermal expansion coefficient data given in Table II for various materials. This probably indicates absence of an interfacial reaction and the interdiffusion of cations between the film and the $SrTiO_3$ substrate.

X-ray diffraction spectra (Fig. 1) of the two films on the YSZ substrate sintered for 5 or 15 minutes show almost single phase 123 superconductor. The XRD patterns of the films on various ceramic substrates fired for 15 minutes are given in Fig. 2. The HTS phase is present in the films on YSZ or MgO. Weak intensity peaks of the most prominent lines corresponding to Y_2BaCuO_5 and $BaCuO_2$ are also seen in the spectra. The peaks for $SrTiO_3$ present in the spectra of ST-1 film are from the substrate. The Y_2BaCuO_5 and $BaCuO_2$ phases, alongwith the HTS phase, are present in the film on alumina substrate probably due to phase separation of the superconducting phase. This is in agreement with the results of Budhani et al[8].

Temperature dependence of electrical resistivity normalized to its value at 100 K for some of the films is shown in Fig. 3. All the films showed metallic behavior in the normal state until a sharp drop in resistance occurred at the onset temperature, T_c(onset). Values of T_c(onset), T_c(R=0), and the transition width, ΔT_c(10-90%), for various films are listed in Table I. The two films ZR-1 and ZR-2 on YSZ substrate baked at 5 or 15 minutes at 1000 ^{o}C showed similar electrical behavior with T_c(R=0) of ~88.1 K and ΔT_c ~1.8 K. During a study of the reaction of $YBa_2Cu_3O_7$ and YSZ in the sintered powder form, formation of $BaZrO_3$ was observed[9] at an annealing temperature of

945 ^{o}C in oxygen according to the reaction:

$$4YBa_2Cu_3O_7 + 6ZrO_2 \longrightarrow 2Y_2BaCuO_5 + 10CuO + 6BaZrO_3 + O_2$$

However, in the present study no $BaZrO_3$ was detected from XRD of the films on YSZ. Tabuchi et al.[11] studied the interface between the $YBa_2Cu_3O_7$ thick film and the YSZ substrate fired at 990 ^{o}C in oxygen. As Ba^{2+} ions diffused into the substrate, parts of the substrate changed to $BaZrO_3$ and parts of the film converted into Y_2BaCuO_5. No CuO could be detected in the film by XRD. In the $YBa_2Cu_3O_7$ thick films on YSZ which had been sintered for 10 min at 1000 ^{o}C in oxygen, the diffusion distance of Zr^{4+} into the film was measured[12] to be ~18 μm from analytical electron microscopy. The penetration depth of Y^{3+}, Ba^{2+}, and Cu^{2+} into the substrate was estimated as ~35 μm. The interface between Y-Ba-Cu-O thin films and YSZ substrates formed by laser deposition at 650 ^{o}C has been investigated[10] by high-resolution transmission electron microscopy and *in situ* resistivity measurements. No additional post annealing heat treatment was done. A distinct interface layer of ~5 nm thickness was observed[10] which had low resistivity. This was in contrast to the MgO and $SrTiO_3$ substrates where the interface oxide compounds showed high resistivity.

The films on alumina showed high onset temperatures, but did not become fully superconducting even at 55 K, the lowest temperature of measurement in the present study. This may be due to the interdiffusion of Al^{3+} into the film as reported by others[7]. Alumina is reported[6] to have a limited solubility in $YBa_2Cu_3O_7$, but chemically decomposes it. The T_c of the unreacted $YBa_2Cu_3O_7$ phase is not affected[15], but the transition becomes broad due to the presence of the decomposition products as impurities. Phase separation of $YBa_2Cu_3O_7$ into $BaCuO_2$ and $Y_2Cu_2O_5$ has been observed[8] in Y-Ba-Cu-O films screen-printed on alumina and sapphire substrates and heat treated for 30 minutes at 1000 ^oC in flowing oxygen. In the $YBa_2Cu_3O_7$ thick film on alumina which had been annealed for 1 h at 950 ^oC in oxygen, the penetration depth of Al^{3+} into the film was measured[12,13] to be ~25 μm using analytical electron microscopy. Severe segregation of Y^{3+}, Ba^{2+}, and Cu^{2+} in the film near the interface was also observed. The following chemical reaction has been proposed[9] between alumina and $YBa_2Cu_3O_7$ when heated at 945 ^oC in oxygen:

$$4YBa_2Cu_3O_7 + 6Al_2O_3 \longrightarrow 2Y_2BaCuO_5 + 10CuO + 6BaAl_2O_4 + O_2$$

However, in the present study no peaks for $BaAl_2O_4$ could be detected in the XRD spectra of the films on alumina substrate.

The two films MG-2 amd MG-3 on spinel which were sintered for 15 and 5 minutes, respectively, showed the same $T_c(R=0)$ of 75.5 K and ΔT_c of 12-13 K. The low T_c and rather large transition width may be due to the interfacial reaction between the film and the substrate and the interdiffusion of magnesium into the film. Mg is known[6] to substitute at the copper sites in the $YBa_2Cu_3O_7$ structure and significantly reduces its T_c. When $YBa_2Cu_3O_7$ was doped with 2 mol% of MgO in place of CuO, its T_c decreased from 91 to 65 K. T_c(onset) values as low as 68 K have been reported[7] for the Y-Ba-Cu-O films on MgO substrates prepared by electron beam codeposition. A possible reason for this low T_c was suggested[7] to be a large amount of interdiffusion of magnesium from the substrate into the film even at the processing temperature of 850 ^{o}C. The extent of this diffusion would be much more at 1000 ^{o}C, the temperature employed in the present study for annealing the films. In the $YBa_2Cu_3O_7$ thick films on MgO which had been sintered for 10 min at 1000 ^{o}C, the penetration depth of Mg^{2+} into the film was measured[12] to be 25-30 μm from analytical electron micrscopy. The penetration distances of Y^{3+}, Ba^{2+}, and Cu^{2+} into the substrate were greater than 40 μm. Chemical interaction between $YBa_2Cu_3O_7$ and MgO has also been studied[9] in the sintered powder form at 945 ^{o}C in oxygen. From powder XRD no new phase was detected. However, enrichment of MgO with Cu and the formation of an apparently glassy Ba-Cu phase was observed[9] from EDAX analysis.

Although, film #ST-1 on $SrTiO_3$ which was sintered for 15 minutes showed excellent properties with T_c(onset) of 91.1 K, T_c(R=0) of 89.1 K, and ΔT_c of 1.6 K, its adhesion with the substrate was poor. In fact film #ST-2 on $SrTiO_3$ which had been fired for 5 minutes completely detached from the substrate during measurements. This may indicate that no chemical reaction or interdiffusion at the film/substrate interface occurred during sintering at 1000 ^oC. However, a study[9] of the chemical reaction of $YBa_2Cu_3O_7$ with $SrTiO_3$ in the compact powder form at 945 ^oC for 5 h in oxygen reported the replacement of Ba by Sr in the HTS and the formation of an unknown phase containing Ba-Ti-Y-Cu. Annealing for longer times at 1000 ^oC would probably improve the film adhesion with the substrate, but may have a detrimental effect on its superconducting behavior.

SUMMARY OF RESULTS

Thick films of $YBa_2Cu_3F_{0.066}O_y$ have been deposited on several ceramic substrates by a screen printing technique. The best film was obtained on YSZ with T_c(onset) of 91 K, T_c(R=0) of 88.2 K, and transition width, ΔT_c(10-90%), of ~1.7 K. Comparison with an earlier study[4] on undoped films showed no advantage for fluorine doping of the films. The film adhesion was good in all cases except on $SrTiO_3$ where the film completely detached from the substrate. This adhesion is probably controlled by the interdiffusion of cations between the film and the substrate during the sintering step.

CONCLUSIONS

Fluorine doping of $YBa_2Cu_3O_{7-x}$ films screen printed on various ceramic substrates does not improve their superconducting properties in spite of the higher T_c and sharpened transition observed in bulk HTS when doped with low concentrations of fluorine.

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TABLE I. Properties of fluorine-doped and undoped $YBa_2Cu_3O_{7-x}$ films screen printed on different substrates, sintered at 1000 °C, and annealed in oxygen for 3 h at 450 °C.

Film No.	Substrate	Sintering time at 1000°C (min)	T_c(K) onset	T_c(K) R=0	ΔT_c(K) (10-90%)	Adhesion
			Fluorine-Doped			
ZR-1	YSZ	15	91	88.2	1.7	Good
ZR-2	YSZ	5	90.6	88.1	1.8	Good
ST-1	$SrTiO_3$	15	91.1	89.1	1.6	V. Poor
ST-2	$SrTiO_3$	5	--	--	--	Detached
MG-2	MgO	15	90.2	75.5	~12	Good
MG-3	MgO	5	91.5	75.5	~13	Good
AL-1	Al_2O_3	15	89.2	<55	--	Good
AL-2	Al_2O_3	5	91.9	<55	--	Good
			Undoped			
ZR-3	YSZ	15	91	88	1.7	Good
MG-1*	MgO	15	96	81	7	Good
5*	Al_2O_3	15	94	66	10	Good

All films were black.
*Results for these films taken from ref. 4.

TABLE II. Mean thermal expansion coefficients of the superconductor and the various ceramic substrate materials

Material	Temperature range (°C)	Mean thermal expansion coefficient, α (°C^{-1})	Reference
$YBa_2Cu_3O_{7-x}$ (HTS)	30–900	16.9×10^{-6}	Hashimoto et al[14]
Alumina (996 Superstrate)	25–800	7.3×10^{-6}	Matl. Res. Corp.
MgO (S-145 Spinel)	25–800	13.5×10^{-6}	Trans-Tech
$SrTiO_3$	30–900	11.1×10^{-6}	Trans-Tech
YSZ[a]	25–1500	$(9.2-10.3) \times 10^{-6}$	CERES

[a]9.5 mol% yttria stabilized cubic zirconia, random orientation

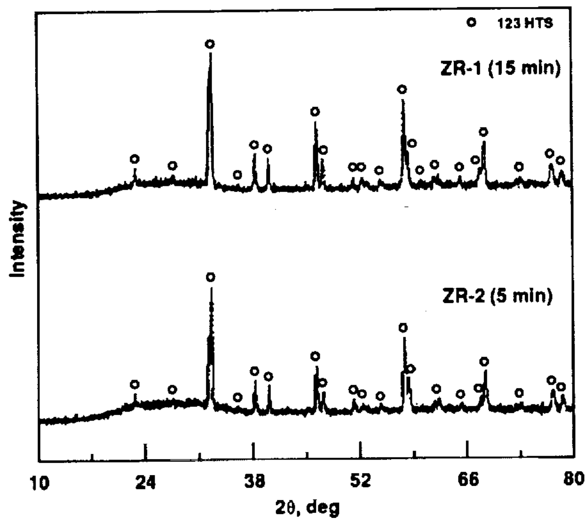

Figure 1.—X-ray diffraction patterns of $YBa_2Cu_3F_{0.066}O_y$ films screen printed on yttria-stabilized zirconia substrate and sintered at 1000 °C in oxygen for 5 or 15 min.

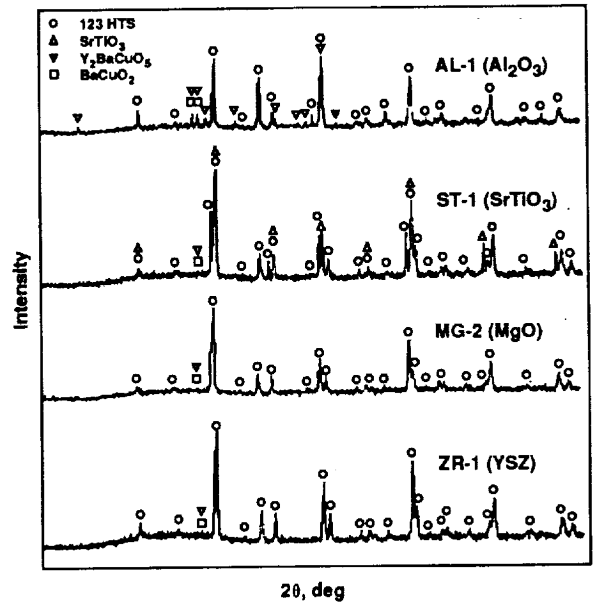

Figure 2.—X-ray diffraction spectra of $YBa_2Cu_3F_{0.066}O_y$ films screen printed on various ceramic substrates and annealed for 15 min in oxygen at 1000 °C.

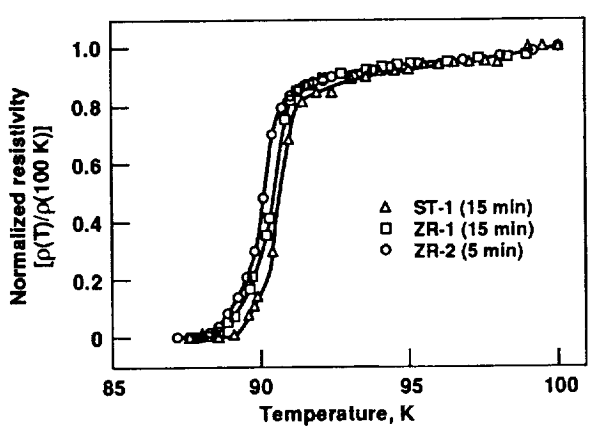

Figure 3.—Temperature dependence of electrical resistivity of fluorine-doped $YBa_2Cu_3O_{7-x}$ films screen-printed on ceramic substrates and baked at 1000 °C in oxygen for the time shown.

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