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THE EFFECT OF ANNEALING ON THE SUPERCONDUCTING PROPERTIES OF RF MAGNETRON SPUTTERED BSCCO FILMS

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Abstract. The effect of conventional (long time) and short time (1 min) post annealing of superconducting properties of $Bi_1Sr_1Ca_1Cu_1O_x$ films deposited by RF magnetron sputtering on MgO, $SrTiO_3$ and Al_2O_3 substrates was investigated.
By long time annealing procedure values of $T_c = 70$–78 K were obtained, while the best results by short time annealing were $T_c \leq 68$ K. But only short time annealing procedure was successfully used to prepare films on Al_2O_3 substrates, demonstrating a superconducting transition.

Резюме. Исследовано влияние процедур продолжительного (стандартного) и кратковременного) (1 мин) отжига на сверхпроводящие свойства пленок $Bi_1Sr_1Ca_1Cu_2O_x$, полученных методом ВЧ магнетронного напыления на подложках MgO, $SrTiO_3$ и Al_2O_3.
С помощью стандартной процедуры отжига получены пленки с $T_c =$ 70–78 K, а при кратковременном отжиге лучшие результаты составляли $T_c \leq 68$ K. Однако, сверхпроводящие свойства пленок на Al_2O_3 проявлялись только после процесса кратковременного отжига.

Since its discovery [1], the Bi-Sr-Ca-Cu-O (BSCCO) superconductor has been a subject of intensive study. It has been shown that superconducting properties of BSCCO films are strongly affected by the deposition and annealing conditions and depend on the substrate surface quality [2–4]. The RF magnetron sputtering is a widely used method for preparing superconducting BSCCO thin films [3,4]. On the other hand this method gives strong inhomogeneity of the thickness and chemical composition of the film on the substrate, depending on the gas composition and the sputtering pressure, and on the substrate temperature [3–5]. The problems of annealing conditions have been discussed by many authors [2–5]. In the two-step preparing process annealing can be carried out in the temperature range 800–900°C in O_2 or air [3–5]. However, the optimal annealing conditions are affected by numerous factors and may be revealed only experimentally.

In this paper we have investigated the conventional (long time) and short time post annealing effects on superconducting properties of BSCCO thin films, deposited on MgO, $SrTiO_3$ and Al_2O_3 substrates by RF magnetron sputtering.

Table 1. The deposition conditions of BSCCO films

	I run	II run
Target	unannealed $Bi_1Sr_1Ca_1Cu_2O_x$ disk, 5 cm diameter	superconducting $Bi_1Sr_1Ca_1Cu_2O_x$ disk, 5 cm diameter
Target-substrate distance	3 cm	3cm
Substrates	MgO (100) $SrTiO_3$ (100)	MgO (100), $SrTiO_3$ (100) Al_2O_3 polycrystal
Sputtering gas	2.6 Pa, pure Ar	7 Pa, pure Ar
RF input power	150 W	220 W
Substrate temperature	150°C	220°C
Film thickness	1 μm	1–2 μm

The detailed description of the experimental equipment has been presented elsewhere [6]. The deposition conditions of two runs are given in Table 1. The composition, the structure and the surface morphology of the films were examined by energy-dispersive X-ray analysis (EDAX), X-ray diffractometer and scanning electron microscopy (SEM). The annealing temperature was measured by Al-Cr thermocouple with ±8°C accuracy. The resistance of the films was measured by four-point method, using indium contacts.

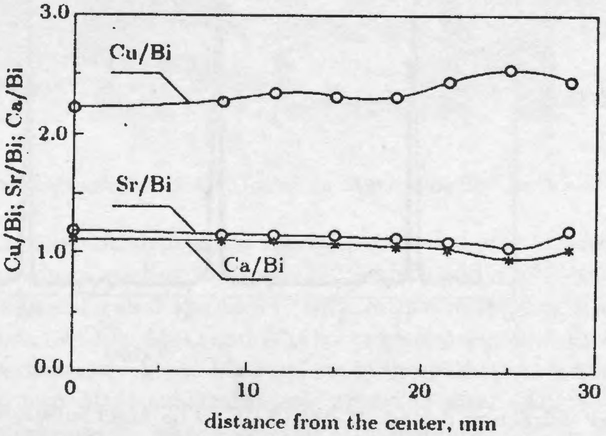

Fig. 1. Radial distribution of the composition of BSSCO film sputtered from superconducting $Bi_1Sr_1Ca_1Cu_2O_x$ target

The film deposition was carried out on substrates, placed under the central region of the target. The atomic composition of these films was equal to that of the target with an accuracy λ 20% (Fig. 1). The as-deposited films were shiny black

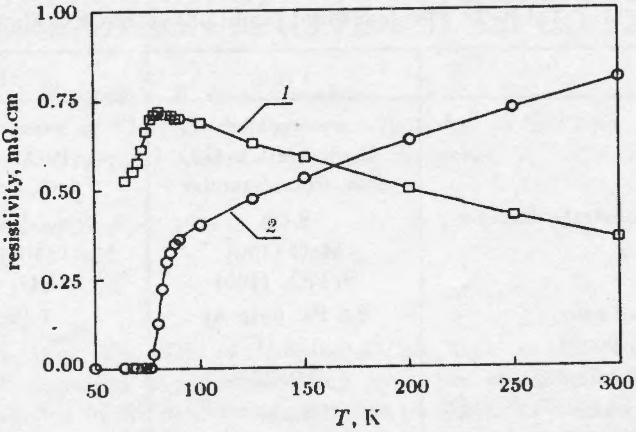

Fig. 2. Resistivity vs temperature curves for BSCCO films on MgO substrate: *1* — film annealed at 850°C for 1 h in O_2; *2* — film annealed at 875°C for 1 h in O_2

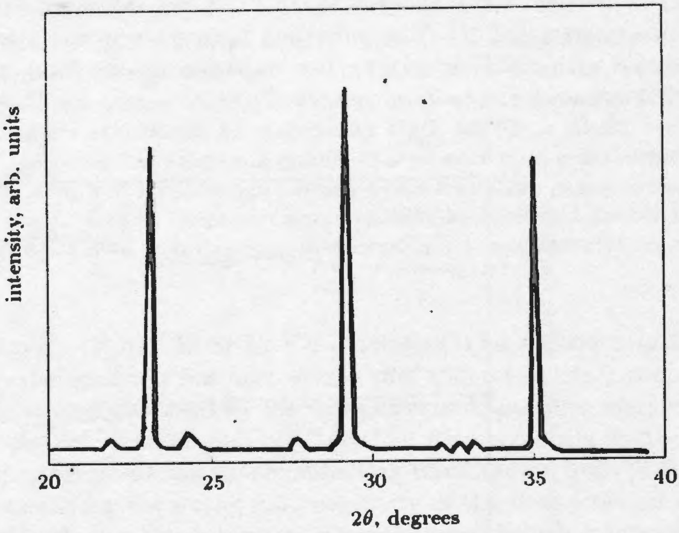

Fig. 3. X-ray diffraction pattern of BSCCO films on MgO substrate annealed for 1 h at 875°C in O_2

and insulating. In order to obtain superconducting properties the films of first run on MgO substrates were annealed in flowing oxygen (0.5 l/min) at temperature 770°C for 1 h, at 840–900°C for 1 h and then slowly cooled to room temperature at a rate of 2°C/min. The surface of the films, annealed at 840–860°C was smooth and dense. The resistance–temperature (R–T) dependence of these films shows a semiconducting type of behaviour (Fig. 2, curve *1*) with a superconducting onset at 78 K and has a low temperature tail. On the other hand, after annealing at 860–880°C, the resistance–temperature curve shows a metallic behaviour and superconducting transition with T_c = 70–78 K (Fig. 2, curve *2*). The surface of these films contains some quantity of randomly distributed defects and voids. The diffraction pattern shows a series of peaks at $2\theta = 23.2°, 29.3°, 35.1°$, indicating that the c-axis of the film is preferentially oriented normally to the substrate surface (Fig. 3). The annealing of the films up to approximately the melting point (880–890°C) changes dramatically the surface quality: a lot of defects and voids appear on the film surface. The diffraction pattern of such a film resembles that of ceramics, SEM photograph of such a film shows needlelike structure of randomly oriented grains (Fig. 4). These films show either metallic or superconducting R–T characteristics with zero resistance temperature of 60–78 K. Similar results were obtained for BSCCO films, deposited on $SrTiO_3$ substrates.

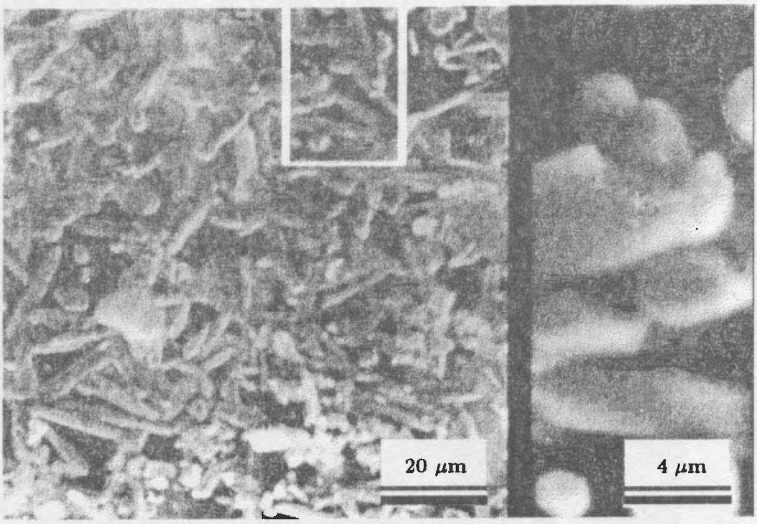

Fig. 1. SEM micrography of BSCCO film on MgO annealed for 1 h at 890°C in O_2

The films of the second deposition run were annealed only for short time (1 min) in air. The heating and cooling rates are 170°C/min and 420°C/min, respectively. At first we have investigated the room temperature resistance R_{300} of three test films (deposited on $SrTiO_3$, MgO and Al_2O_3) annealed sequentially for a short time at various temperatures (Fig. 5). Minimal room temperature resistance of BSCCO films on $SrTiO_3$ and MgO substrates was observed after (850–880°C) annealing and on Al_2O_3 substrates — after (700–750°C) annealing.

The most appropriate annealing temperature for the films, deposited on MgO and $SrTiO_3$ substrates was found to be 860–875°C. The films, annealed under such conditions, consist of platelets, oriented nearly parallel to the surface of the substrate (Fig. 6) and demonstrate metallic character of R–T dependance. But only by short time annealing procedure we were not able to obtain films with zero

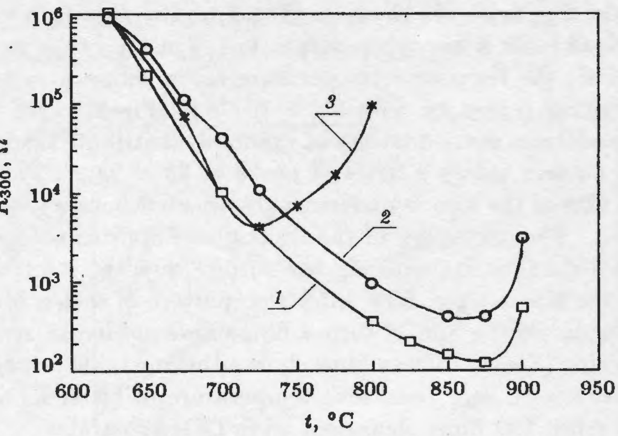

Fig. 2. Effect of the annealing temperature on the room temperature resistance of the BSCCO films on MgO (curve *1*), $SrTiO_3$ (curve *2*) and Al_2O_3 (curve *3*) substrates

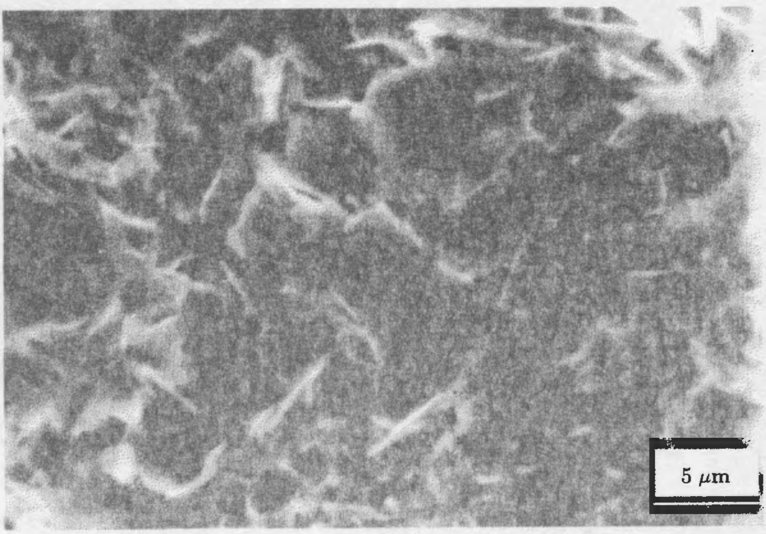

Fig. 3. SEM micrography of short time annealed (at 870° C in air) BSCCO film on $SrTiO_3$

resistance temperature above 68 K. On the other hand, after short time annealing in most cases we observed a marked change of electrical behaviour and an increase of zero resistance temperature of the films from the first run, preannealed at low temperature (Fig. 7).

The annealing temperature 860° C is too high to prepare BSCCO films on Al_2O_3 substrates, because at this temperature an interfacial reaction between the film and the substrate takes place. Therefore, we annealed such films at $T < 740$°C. Usually, the electrical behaviour of these films has demonstrated two-step superconducting transition (caused by the presence of 80 K and 20 K superconducting phases) with

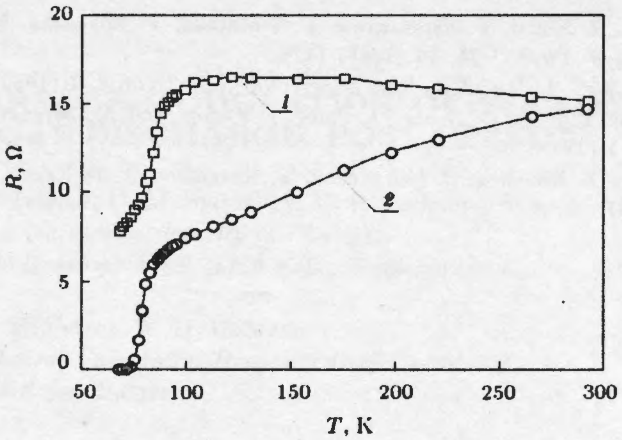

Fig. 7. Resistance vs temperature curves for BSCCO films on $SrTiO_3$ substrate: *1* — annealed at 840°C for 1 h in oxygen atmosphere; *2* — the same film postannealed at 870°C for 1 min in air

zero resistance temperature ~ 5 K.

Finally, we examined the possibility for preparing BSCCO superconducting narrow strips by means of a postannealing procedure. A strip of BSCCO film (100 μm) wide and 1 mm long was deposited through stainless steel mask on MgO substrate. After a long time annealing process, this strip showed zero resistance temperature 70 K. For more narrow lines (50 μm) we have not observed full superconducting transition because such lines were destructed by defects, introduced during annealing procedure.

Conclusions

(*i*) A remarkable advantage of the superconducting target in comparison with the unannealed one with the same composition was not found.

(*ii*) The optimum annealing temperature for the films could be found measuring the room temperature resistivity of only one sample, annealed at increasing values of temperature.

This method is particularly useful for a new annealing setup or new film/substrate combination.

(*iii*) We were not able to obtain high value of T_c for BSCCO film only by short time annealing. But short time annealing at higher temperature after a long time procedure considerably increases the T_c values. Besides, with this procedure the better film surface quality is obtained.

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