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(Y-Er)-Ba-Cu-O superconducting thin films obtained ex-situ: toward submicrometric patterning by electron beam lithography

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Abstract

We have grown (Y-Er)BaCuO superconducting thin films on $SrTiO_3$, with thicknesses ranging from 250 to 7500 A. The superconducting films have been obtained from amorphous precursors deposited by rf magnetron sputtering from a single mosaic target made of (Y-Er), BaF_2. An ex-situ annealing procedure has been used. The critical temperatures depend on their structural connectivity and thickness. The choice of performing the annealing ex-situ made possible to write, by using the electron beam lithography and the lift-off technique, test lines as narrow as 130 nm for the precursor film and useful bridges in the range of one micron for the annealed sample.

Introduction

The recent progress in the preparation of high T_c superconducting thin films makes the dream of using them to produce superconducting devices at 77 K much more realistic. In particular, impressive results have been obtained by in-situ growth of superconducting thin films by laser ablation[1-2] and magnetron sputtering[3-5] in a relatively high oxygen pressure, starting from a ceramic bulk target. The very high critical temperature obtained for ultra-thin films opens new possibilities for patterning, because their thickness is now well below the minimum required, < 1500 A for the use of the electronic resist like PMMA. However, the samples should be not only very thin but also extremely flat and homogeneous in order to obtain resolutions that make the use of the electron beam litography worthwhile. When the films are composed by, even well connected, crystallites (either c or a oriented) it becomes very difficult to obtain submicrometric definition of the pattern bacause the crystallites are normally etched as a whole; this effect has been clearly shown in a recent paper, at least as far as the optical lithographic processes are concerned[6]. In that paper we have also shown that a possible alternative to the wet-etching of in-situ grown superconducting thin films is offered

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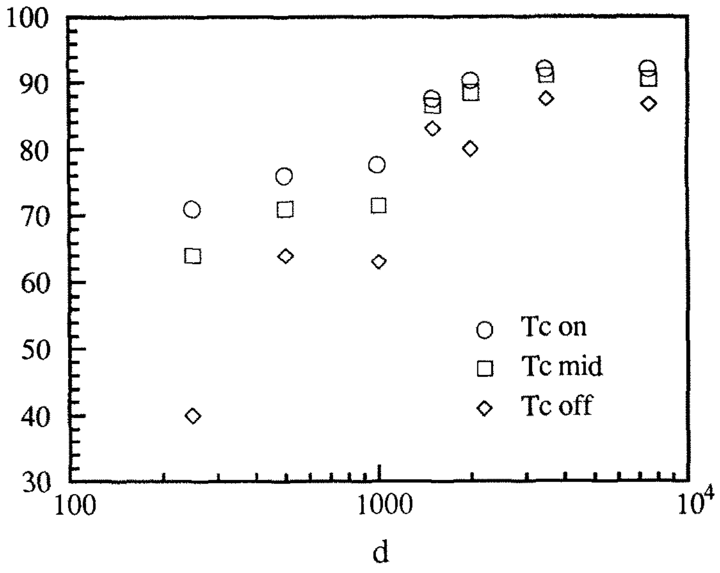

Fig. 1) Variation of the critical temperature (T_c onset, T_c midpoint, T_c offset taken at R=0) as a function of sample thickness d for our (Y-Er)BCO thin films grown on (001) $SrTiO_3$ substrates.

by the wet etching of the amorphous precursor films obtained by magnetron sputtering, following the BaF_2 route. Here we show how the lift-off procedure applied to the same precursor films could lead to micrometric (and hopefully submicrometric) pattern definition. This technique could not be applied to films grown in-situ and this prompts new interest for the ex-situ preparation processes of high T_c thin films. In the following we will deal briefly with our present state-of-the-art in the ex-situ preparation of (Y-Er)BaCuO thin films, and with some very preliminary results concerning the electron beam patterning of these films.

Experimental and Discussion

Our superconducting (Y-Er)BaCuO thin films are obtained by annealing ex-situ amorphous films grown by magnetron sputtering from a single mosaic target composed by (Y-Er), BaF_2 and Cu. The precursor films show the correct stoichiometry, 1:2:3, on a very large area of 12 cm in diameter. The ex-situ annealing has been performed using a standard two-plateau temperature profile. More details on the sample preparation can be found in refs.7-8.

Thin films have been prepared in the thickness range 250-7500 A and all are superconductors although their characteristic critical temperatures decrease with the thickness d, see fig. 1. The films have different structure for different d, see fig. 2: c-oriented (c-axis perpendicular to the plane of the substrate) are obtained for $d \leq 2000$ A; a-oriented thin films from the surface and for almost the whole thickness of the sample are obtained for $2000 \leq d \leq 4000$ A; randomly oriented thin films, are finally obtained for $d > 4000$ A. Their transport properties and the detailed discussion of fig. 1 are reported in refs.6-9, here we would like only to remind briefly that the decrease of the characteristic critical temperature of the thin films, fig. 1, can be ascribed to two concomitant causes:

a) the oxygen desorption that create a gradient of oxygen concentration in the proximity of the surface; the T_c onset should be particularly sensitive to this effect;

b) a possible interdiffusion at the substrate interface; this should affect mainly the value of the T_c offset, expecially for very low thin films: < 500 A.

These two effects may also explain while for the samples produced in-situ[1-5],by magnetron sputtering, the breakdown of the characteristic critical temperature is displaced towards lower values of d. In fact these films are produced in an oxygen atmosphere at a rather high pressure of ionized particles, and at a substrate temperature (700 °C), relatively low respect to that of our highest plateau of the annealing temperature profile: 850 °C. Although our ex-situ preparation procedure should be improved to obtained results comparable to those of refs.3-5, in the following we will show the advantages that it may offer in the patterning of thin films. The first evident one is that, having the possibility to pattern the amorphous precursor films, very precise pattern profiles can be obtained by wet etching, see fig. 3a, also when the final superconducting films are relatively thick, > 1000 A, and their SEM pictures clearly show the presence of crystallites after the annealing process (and this without using very expensive apparatus like lasers or ion guns)[10-13]; this fact turns out to be extremely important in the field of the optical patterning and are discussed more extensively in ref.6.

The second advantage is the possibility of using the lift off technique (fig. 3). This technique can be used coupled either to an optical or to the electron beam definition of the pattern. As shown in fig. 3, one has first to spin the resist on the substrate, then grow the precursor film after the pattern definition, and finally remove the resist. In figures 4a and 4b we show what the film looks like before and after the resist removal. Using this technique we have been able to define

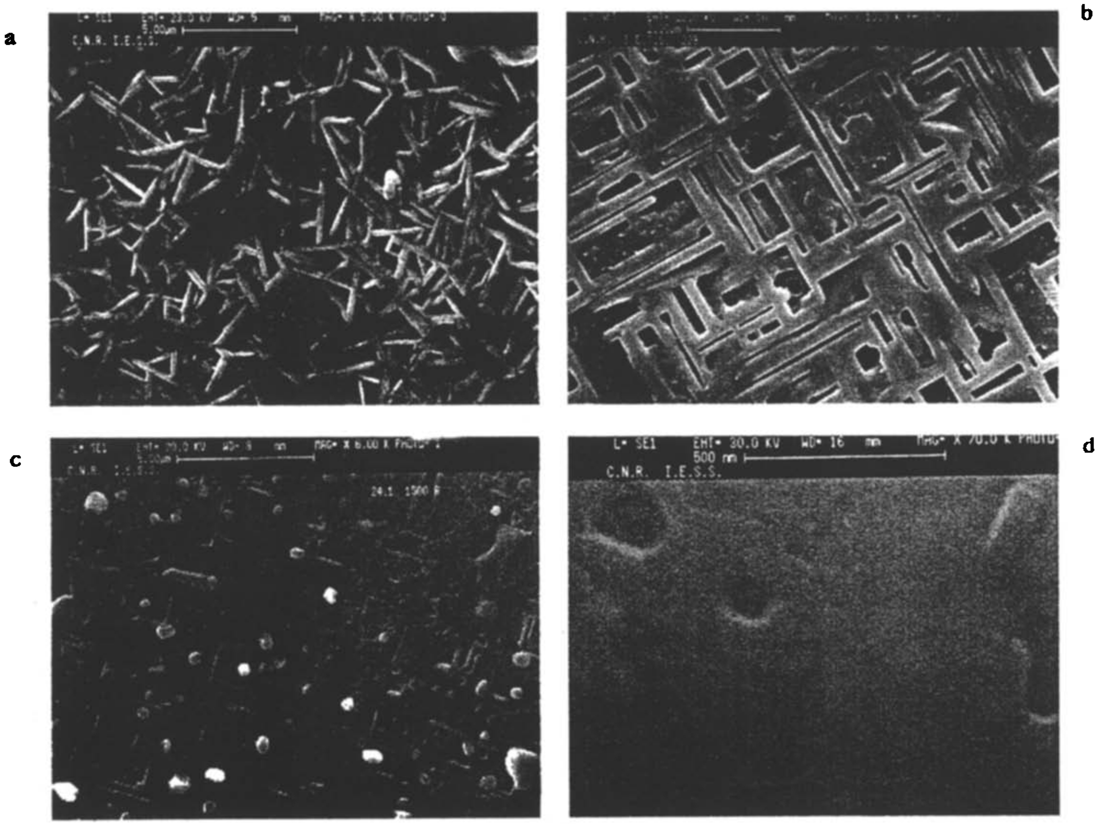

Fig.2) SEM pictures of 4 samples having different thickness d:a) d=7500 A, b) d=3500 A, c) d=1500 A, d) d=600 A.The cross-linked structure is formed by crystallites with the a-axis perpendicular to the plane of the substrate; the c-axis lies along the shortest dimension of the crystallites; the different scale of the plots has been chosen in order to make some of the structures more visible.

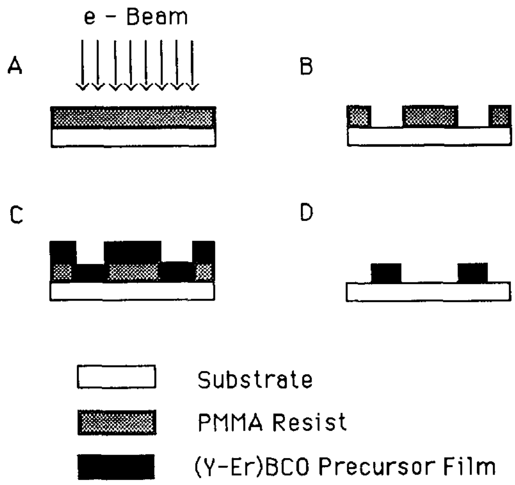

Fig. 3) Example of patterning made by lift-off process

very narrow and small structure on the precursor films; in fig. 5 some SEM pictures of test patterns are shown. Up to now, however, we have not been able to preserve the same degree of definition after the ex-situ annealing, only lines of about 1 μm mantaining a satisfactory degree of definition; that is to say, lines only slightly narrower of what we obtained by optical litography. What happens is that the more narrow lines tend to break because of clustering, see fig. 6. A better definition of submicrometric structure could be hopefully obtained by modifying the annealing conditions and by varing the thickness of the samples. Work is in progress along these lines.

Conclusions

In conclusion, we have shown that by patterning the amorphous precursor films one may obtain in a near future very narrow lines of YBCO. This will be particularly interesting for the design of novel superconducting devices at 77 K. Nevertheless we are still in the preliminary stage of this research and much more work is needed in order to optimize the ex-situ annealing conditions both to improve the quality of the ultra-thin films and to avoid clustering during the formation of the perovskite structure.

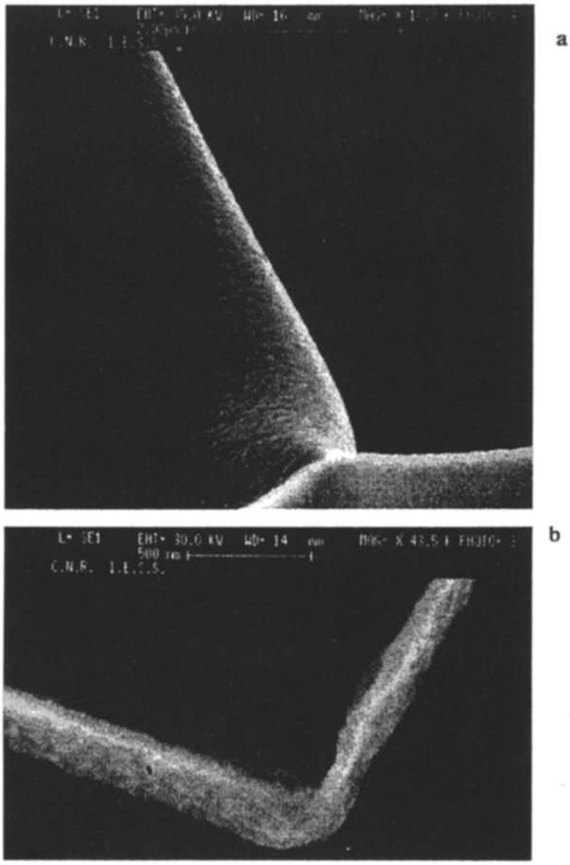

Fig. 4) YBCO precursor thin film a: before the lift-off process (the resist is the brightest area); b: after the lift-off (the brightest area corresponds to the edge of the film)

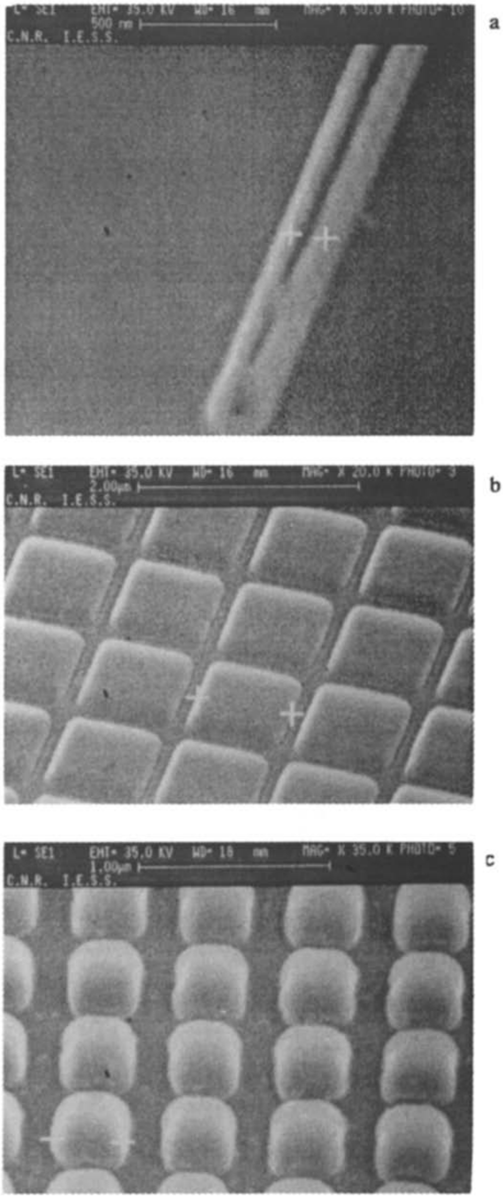

Fig.5) Examples of submicrometric structures patterned on the precursor films The distances between the crossed points are respectively: a - 130 nm; b - 880 nm; c - 380 nm.

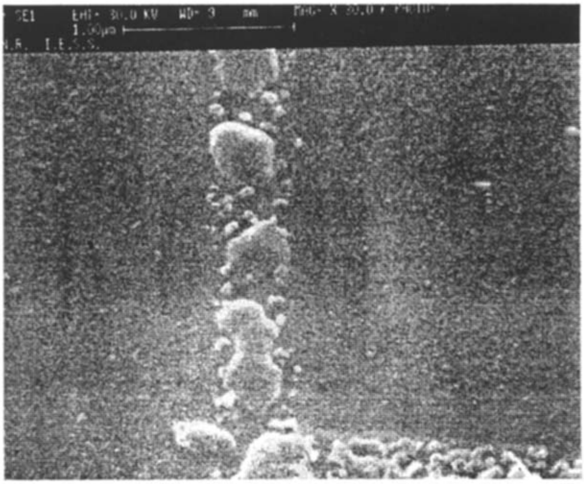

Fig. 6) Example of clustering occurring during the annealing in the case of the thinnest lines.

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