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Effect of processing conditions on superconductive properties of laser-deposited YBCO thin films

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Thin superconductive films of $YBa_2Cu_3O_{7-x}$ have been deposited on (1 0 0) single crystal $SrTiO_3$ substrates by using technique of ArF pulse excimer laser evaporation of bulk YBCO target in a vacuum, followed by slow cooling in an oxygen atmosphere. Thin-film properties are strongly influenced by the processing conditions. The effect of pulse repetition rate, beam power, beam size on the target surface and oxygen pressure on the surface morphology and superconductive properties of deposited films has been investigated. Film characterization has been performed by using X-ray diffractometry, scanning electron microscopy and four-point probe electrical instruments.

1. Introduction

Pulsed laser deposition has been demonstrated to be a promising technique for producing high-quality superconducting Y–Ba–Cu–O films [1–4]. One of the most important advantages of using laser ablation of a bulk Y–Ba–Cu–O target is a good control of stoichiometry. The quality of deposited films is, however, strongly dependent on various processing conditions such as laser beam spot size and energy density, pulse repetition rate, substrate temperature and ambient oxygen pressure. The aim of the investigation was to find optimal conditions for growing best-quality superconducting films.

2. Experimental procedure

The experimental apparatus is shown in Fig. 1. An ArF pulsed excimer laser (Lambda Physik EMG 201MSC) with wavelength 193 nm and pulse duration 24 ns was used for ablation. The stainless steel vacuum chamber was equipped with rotation and diffusion pumps, rotating target holder and heated substrate holder. A ring electrode operating at a positive bias of 300–400 V was placed between the target and the substrate. The stream of high-purity oxygen regulated by a needle valve was directed at the substrate. The laser beam was focused by a lens; beam size at the target surface could be regulated by changing lens-to-target distance.

During ablation the target was rotated at a speed of 12 r.p.m. and a simultaneous movement of the lens mounted at a computer controlled x–y table allowed the target to be scanned in the radial direction. The combination of target rotation and radial beam scan created a spiral track on the target surface and resulted in a uniform ablation of the target. Ceramic pellets of Y–Ba–Cu–O composition prepared by a conventional sintering procedure at the Israel Institute of Ceramics and Silicates were used as a target. An X-ray diffractogram obtained from a typical pellet contained predominantly peaks of superconducting orthorhombic phase of $YBa_2Cu_3O_{7-x}$ but also revealed the presence of small amounts of CuO and Y_2BaCuO_5 (Fig. 2). The typical temperature of superconductive transition, T_c, of the target material was 90 K (Fig. 3). Deposition was performed on (1 0 0) $SrTiO_3$ substrate glued to the heater with silver paint for better thermal conductivity. An X-ray diffractogram taken from a typical substrate (Fig. 4) contains only reflections of different order (and of different wavelengths present in the tube spectrum) from the surface plane (1 0 0). Substrate temperature was controlled with two Pt/Pt + 13% Rh thermocouples. By using displacement in two perpendicular directions, as shown in Fig. 1, the substrate can be moved in the direction perpendicular to the target surface in order to change the target-to-substrate distance.

A typical experiment was carried out as follows. The chamber was evacuated to the base pressure of 10^{-5} torr and the substrate was heated to the desired temperature. Prior to the laser ablation, the oxygen pressure in the chamber was increased to 0.2 torr and then maintained at this level during all deposition processes. On completing deposition, the chamber was filled with oxygen to the ambient pressure of 1 atm, the substrate was cooled to 420 °C, held at that temperature for 30 min, and then further cooled to room temperature at the same oxygen pressure.

The electrical resistance of the deposited films as a function of temperature was measured by the four-probe technique in liquid nitrogen. The phase composition of the films and their preferred crystallographic orientation were determined by X-ray

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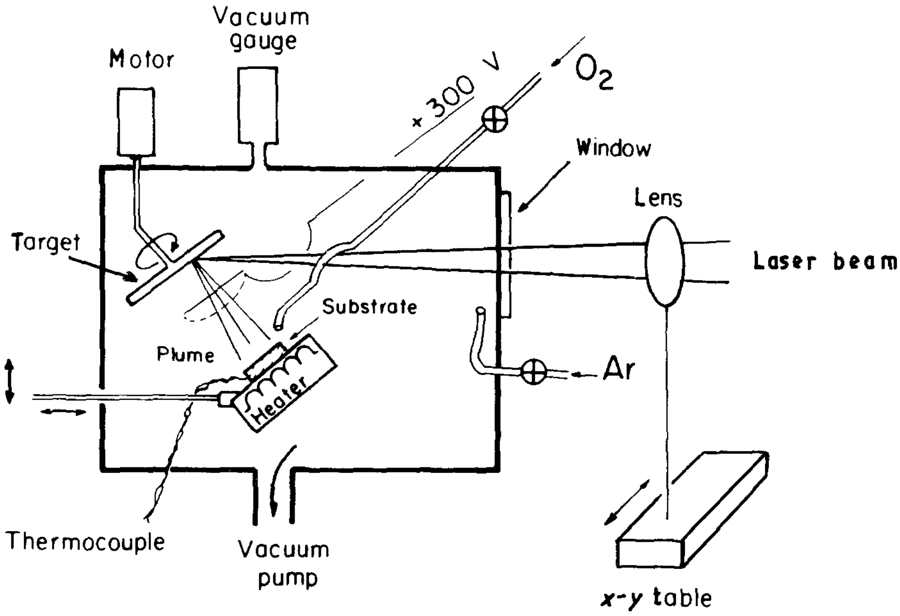

Figure 1 The experimental apparatus.

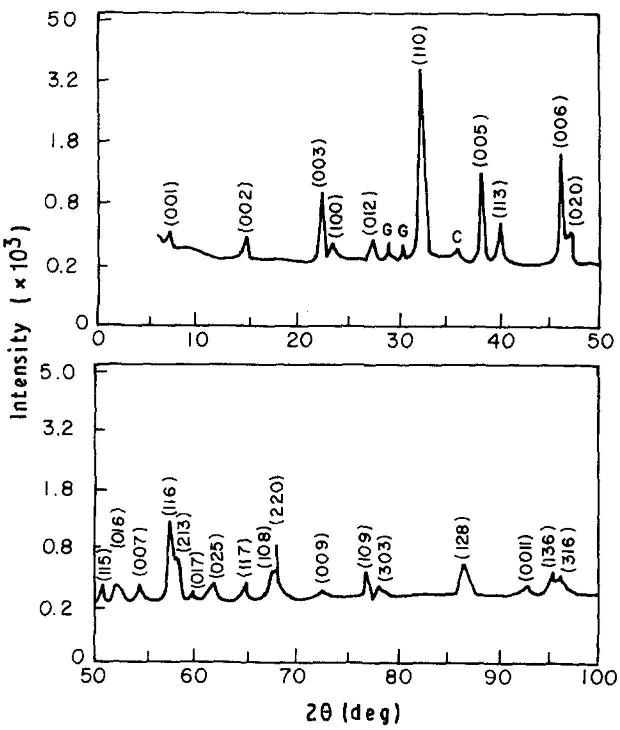

Figure 2 X-ray diffractogram of target Y–Ba–Cu–O material. G, Y_2BaCuO_5 reflections; C, CuO reflections, other reflections belong to $YBa_2Cu_3O_{7-x}$.

diffractometry and film surface morphology was observed by scanning electron microscopy.

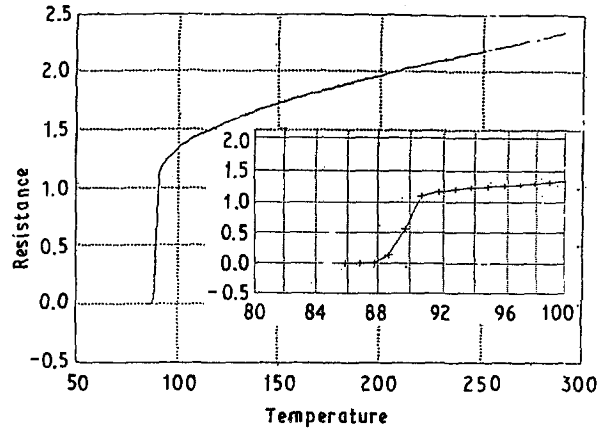

Figure 3 Resistivity versus temperature curve for the target material.

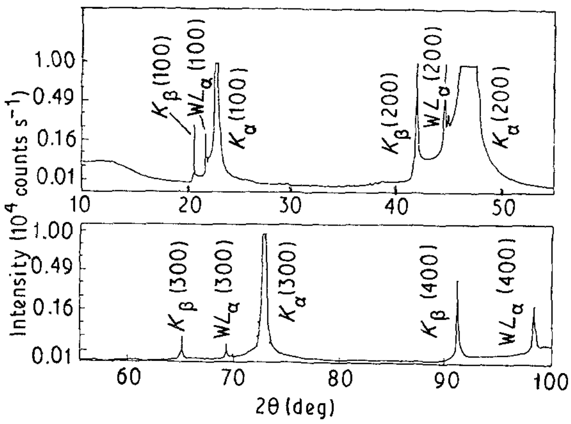

Figure 4 X-ray diffractogram of (1 0 0) $SrTiO_3$ substrate.

3. Effect of deposition conditions on film properties

The conditions used in eight experiments on laser deposition are summarized in Table I. The results of conductivity measurements as well as X-ray diffractograms obtained from deposited films are presented in Figs 5 and 6, respectively. Some conclusions concerning the effect of deposition conditions on film quality can be drawn by comparing thickness, electrical properties and phase composition of films grown in conditions characterized by different combinations of various deposition parameters, such as beam size, beam energy density, deposition temperature, oxygen pressure, pulse rate, etc.

TABLE I Experimental deposition conditions

	Experiment							
	1	2	3	4	5	6	7	8
Beam spot size (mm^2)	10	0.5	0.5	0.5	10	10	10	0.5
Energy density, ($J\ cm^{-2}$)	1.5	8	8	8	1.5	1.5	1.5	8
Oxygen pressure during cooling (torr)	10^3	10	0.2	10	10^3	10^3	10^3	10
Pulse frequency (Hz)	1.5	1.5	1.5	7	1.5	1.5	1.5	1.5
Bias potential (V)	+ 400	+ 300	+ 300	+ 300	–	+ 400	+ 400	+ 300
Substrate temperature (°C)	730	730	730	730	730	660	500	400
Total number of pulses	5×10^3	5×10^4	5×10^4	5×10^4	5×10^3	5×10^3	5×10^3	5×10^4
Deposition rate ($nm\ s^{-1}$)	0.3	0.015	0.015	0.07	0.3	0.3	0.3	0.015
Film thickness (μm)	1	0.5	0.5	0.5	1	1	1	0.5

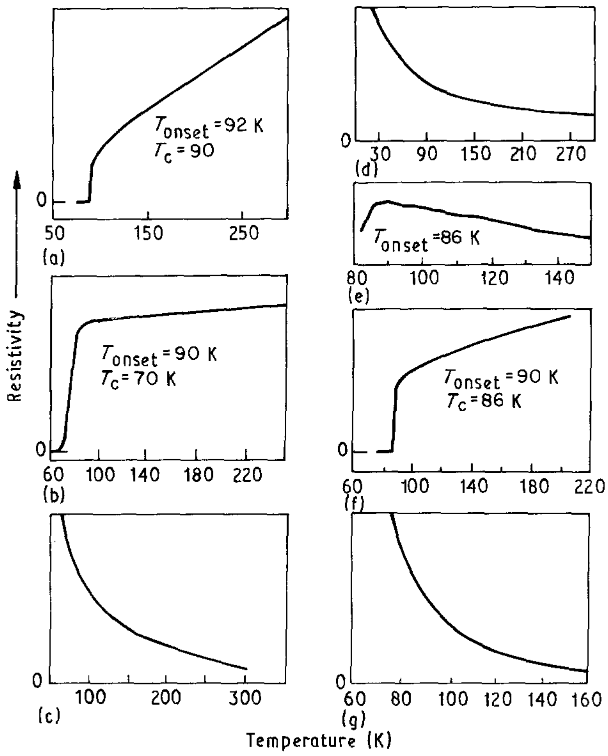

Figure 5 Resistivity versus temperature curve for the deposited films. (a)–(g) Experiments 1–7, respectively, as in Table I.

3.1. Laser-beam size and energy density

Two different sizes of laser-beam spot on the target surface were used in the experiments: a spot size of about 0.5 mm^2 in the case of a focused beam and a spot size of about 10 mm^2 produced by a defocused beam. Because a lower laser power was used with the focused beam, the change in the beam energy density was less drastic: from 8 $J\ cm^{-2}$ in the case of a focused beam spot to 1.5 $J\ cm^{-2}$ in the case of a defocused beam spot. As can be seen from Table I, at a given pulse frequency (1.5 Hz), the average film deposition rate was 20 times higher in the case of the defocused beam, i.e. it was directly proportional to the ablated area of the target and not to the amount of the beam energy hitting the target during each pulse. As a result, only 5000 pulses were needed in order to deposit film as thick as 1 μm with a larger, defocused beam spot.

Films grown in Experiments 1 and 2 (Table I) demonstrate high onset temperatures of superconductive transition (92 and 90 K, respectively) but zero conductivity temperature, T_c, for Film 2 (70 K) is lower than for Film 1 (90 K; the reason for this difference will be discussed below). Both films give diffractograms (Fig. 6a, b) containing, together with 0 0 *l* peaks due to epitaxially grown orthorhombic film, also a weak 1 1 0 peak which represents the strongest reflection from polycrystalline $YBa_2Cu_3O_{7-x}$. In our opinion, the 110 peak, which is more pronounced in Film 2, is due to the presence of small polycrystalline particles incorporated into the deposited films which are seen in SEM image (Fig. 7). These particles seem to be target debris produced by laser-beam pulses, especially at higher energy densities corresponding to a focused beam, and incorporated into a growing film. In addition, Film 2 also shows reflections belonging to $BaTiO_3$ which forms as a result of interaction between the grown film and the substrate at high deposition temperatures (730 °C for both Films 1 and 2). The presence of $BaTiO_3$ in Film 2 can only be ascribed to the fact that the deposition time for this film was increased ten-fold in comparison with that for Film 1, in order to compensate for a very low deposition rate in the case of the focused beam.

3.2. Oxygen pressure during the cooling stage

Superconductive properties of $YBa_2Cu_3O_{7-x}$ depend on oxygen stoichiometry in the lattice [5], with higher oxygen contents to provide better results. While in all our experiments the deposition was always performed at an oxygen pressure of 0.2 torr, three different levels of oxygen pressure were tried during the cooling stage (see Table I): 10^3, 10 and 0.2 torr. The much lower T_c obtained in Experiment 2 in comparison with Experiment 1 can be ascribed to a lower oxygen pressure (10 instead of 10^3 torr). The suggestion is confirmed by a systematic shift in positions of X-ray diffraction peaks obtained from Film 2; the direction of the shift indicates a higher *c*-value of the lattice caused by a lower oxygen content in the lattice. In order to verify the role of the ambient oxygen pressure, Experiment 3 was performed under conditions similar to Experiment 2

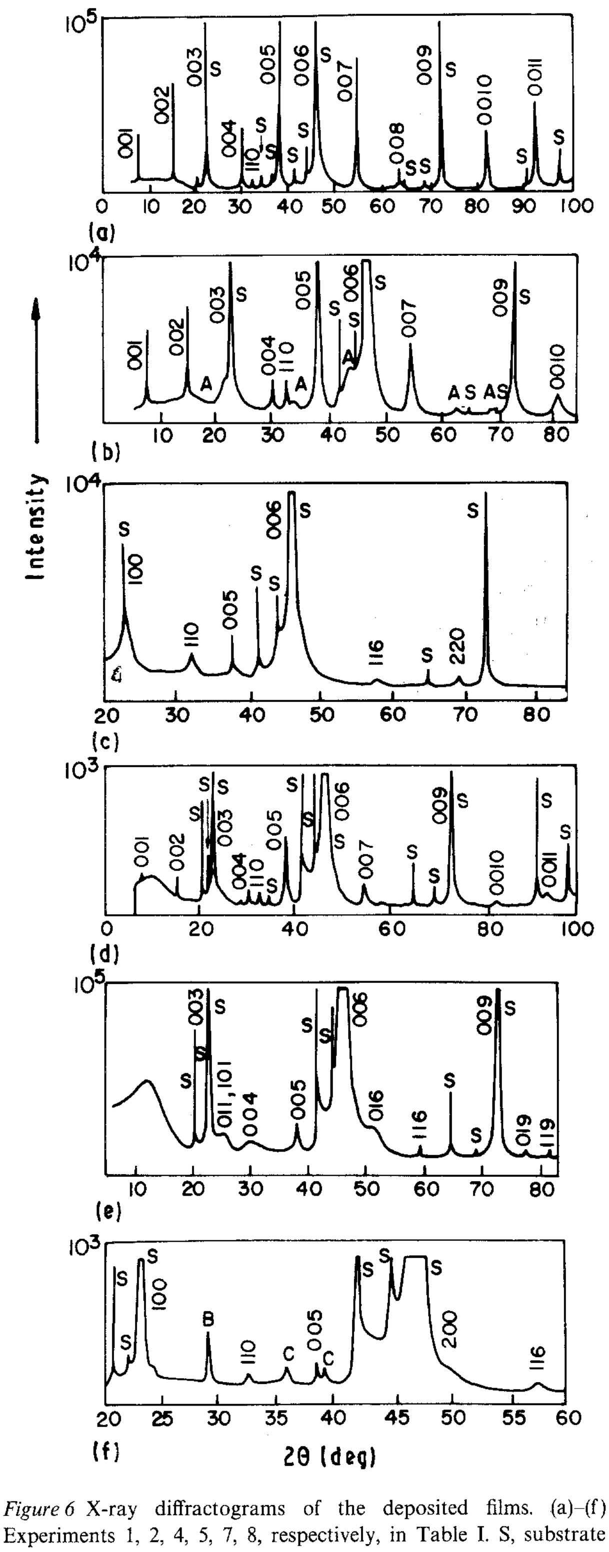

Figure 6 X-ray diffractograms of the deposited films. (a)–(f) Experiments 1, 2, 4, 5, 7, 8, respectively, in Table I. S, substrate reflections; A, $BaTiO_3$ reflections; B, Y_2BaCuO_5 reflections; C, CuO reflections.

except that cooling was done at an even lower oxygen pressure of 0.2 torr, i.e. at the same oxygen pressure as during film deposition. It was found that film obtained under these conditions had no superconductive transition at all (Fig. 5).

3.3. Pulse repetition rate

All deposition experiments in this study were performed at a pulse frequency of 1.5 Hz except Experiment 4 where the pulse frequency was 7 Hz, with other conditions being similar to those in Experiment 2. The

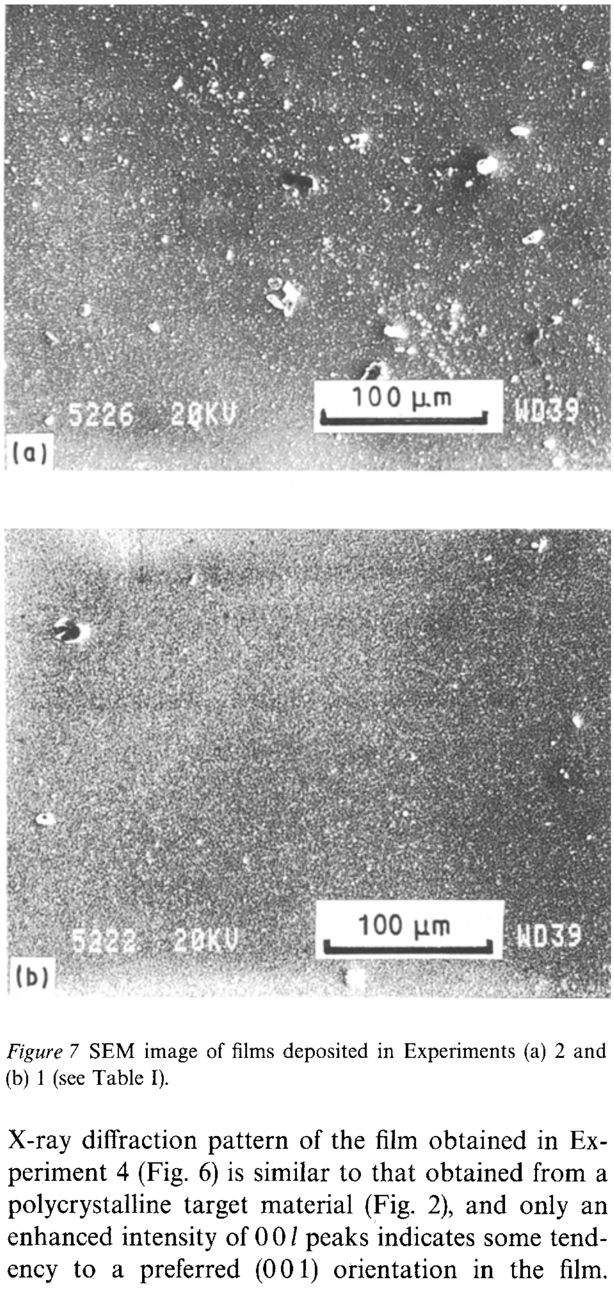

Figure 7 SEM image of films deposited in Experiments (a) 2 and (b) 1 (see Table I).

X-ray diffraction pattern of the film obtained in Experiment 4 (Fig. 6) is similar to that obtained from a polycrystalline target material (Fig. 2), and only an enhanced intensity of 0 0 *l* peaks indicates some tendency to a preferred (0 0 1) orientation in the film. However, unlike the target material or the film obtained in Experiment 2, the film deposited at the pulse frequency of 7 Hz was non-metallic and no superconductive transition took place (Fig. 5). It seems that the (0 0 1) preferred orientation, with Cu–O planes aligned parallel to the substrate surface, is a necessary condition for superconductive behaviour of deposited $YBa_2Cu_3O_{7-x}$ films. It is not, however, clear for what reason a higher pulse repetition rate has an adverse effect on the preferred orientation of the deposited film. Although the obtained deposition rate in Experiment 4 (0.07 nm s^{-1}) was almost five times as high as in Experiment 2, deposition rates below 0.1 nm s^{-1} are considered [4] sufficiently low to provide well-oriented growth of the deposited film. On the other hand, a fully oriented and superconducting film obtained in Experiment 1 was grown with the deposition rate as high as 0.3 nm s^{-1}.

3.4. Bias potential

An introduction of a positively biased electrode between the target and substrate during laser deposition at a low oxygen pressure resulting in the formation of O_2^+ ions containing plasma has been found [3] to assist the deposition process and enhance the oxygen content of the deposited film, therefore improving its superconducting properties. In addition, partially ionized beam deposition is also beneficial for epitaxial film growth [6].

In the present study, all experiments on laser deposition were performed with a positive potential of 300 or 400 V applied to a ring electrode. Only in one experiment (5 in Table I) which otherwise was similar to Experiment 1, was the deposition performed without any applied bias. The corresponding diffraction pattern (Fig. 6) contains $0\,0\,l$ peaks (together with the 1 1 0 reflection "forbidden" in the case of a perfect epitaxial growth) but, compared to the pattern obtained from Film 1, all $0\,0\,l$ peaks except those superimposed by substrate reflections (0 0 3, 0 0 6, 0 0 9) are weak and broad indicating that in spite of a relatively good epitaxy the deposited layer is imperfect, probably, due to variations in oxygen content. (Note that the intensity scale is different in diffractograms of Films 1 and 5 in Fig. 6, as can be seen from the background level or the height of some weak substrate peaks obtained in CuK_β or WL radiations.) The film grown without bias potential also demonstrates deteriorated electrical properties (Fig. 5).

3.5. Deposition temperature

No appreciable effect of deposition temperature in the range 660–730 °C was found in several experiments performed with the use of a defocused beam and under other conditions similar to Experiment 1. However, when deposition was performed at 500 °C (Experiment 7, Table I) the obtained film did not exhibit superconductive transition and showed a non-metallic behaviour of resistivity versus temperature (Fig. 5). Its diffractogram (Fig. 6), like others of non-superconductive films, is characterized by a lower intensity of $0\,0\,l$ peaks and also contains some weak $h\,k\,l$ peaks with l-values much higher than $(h + k)$ values, the latter indicates an imperfect epitaxy of the film. The film deposited at 400 °C with a focused beam (Experiment 8 in Table I) contains not only orthorhombic $YBa_2Cu_3O_{7-x}$ but also CuO and Y_2BaCuO_5 (Fig. 6).

4. Conclusions

1. Good superconducting films ($T_c = 90$ K, $\Delta T = 2$ K) have been epitaxially grown on $SrTiO_3$ substrates by excimer laser ablation.
2. The film deposition rate was found to be directly proportional to the area of the beam spot on the target surface and not to the amount of the beam energy transmitted to the target with each pulse.
3. A long deposition time at high substrate temperatures results in the presence of $BaTiO_3$ due to barium diffusion from the film to the $SrTiO_3$ substrate.
4. The use of an ambient oxygen pressure lower than 1 atm during the cooling stage results in lower transition temperatures or a complete loss of superconductivity.
5. A high pulse frequency (7 Hz) has an adverse effect on preferred orientation and superconductivity of deposited films.
6. Introduction of a positive bias potential between the target and substrate results in better superconductive properties of the film.
7. Substrate temperatures in the range 660–730 °C have no appreciable effect on film superconductivity. A temperature decrease to 500 °C or below, results in non-superconducting films.

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