

# The study of the structural and superconducting properties of YBaCuO films produced by laser ablation method

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**Abstract.** Microstructure and oxygen stoichiometry of YBaCuO films manufactured by laser ablation are investigated. Dependence of the specific electrical resistivity and superconducting parameters of films on microstructure and oxygen stoichiometry is demonstrated. Conditions of deposition are determined, under which films with minimum microstructure defects and good conducting properties are formed. It was found that the concentration of oxygen atoms in the deposited film on the SrTiO<sub>3</sub> surface changes non-linear with the substrate temperature increasing. Also the stoichiometry of the films was calculated and their chemical composition was determined.

## Introduction

A perspective material of the present-day cryoenergetic is high-temperature superconductor (HTSC) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBaCuO) in form of films on a variety of dielectric substrates [1]. So the investigation of the relationship between microstructure and superconducting characteristics of YBaCuO films has the practical interest. It is quite clear that the main superconducting properties of the films (critical temperature  $T_c$ , width of superconducting transition  $\Delta T_c$ , and density of critical current  $J_c$ ) depend on how ideal the microstructure of the resulting films is. This fact is mainly determined by the pinning force on the microstructure imperfections. Planar defects of YBaCuO films microstructure favor the formation of grain interlayers with distortion of the element stoichiometry, including primarily that of oxygen. On the other hand, critical temperature  $T_c$  and width  $\Delta T_c$  of the superconducting transition in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> are functions of the oxygen stoichiometry (7-x) [2,3]. Therefore, an important issue in the formation of superconducting films is the solution of a problem of possible variation of composition, microstructure and superconducting properties of a multiphase composite material.

## Methods and Results

In this paper the structural properties and superconducting characteristics of YBaCuO films produced by laser ablation on a SrTiO<sub>3</sub> (100) single crystal substrate are studied.

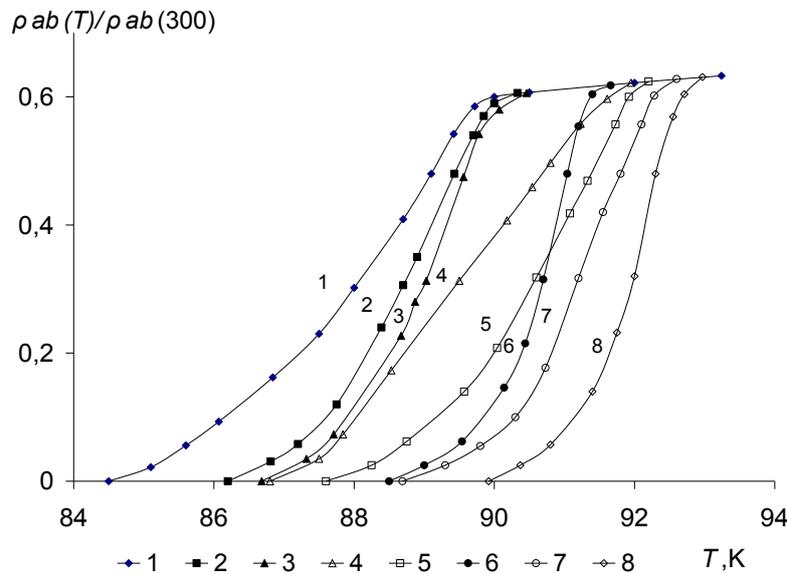
For the films deposition a universal laser facility was used. It consists of two lasers, a universal vacuum station, a system of laser emission control, and a system of substrate temperature control  $T_s$  control. The films were deposited by evaporation of the targets by two crossed YAG-Nd<sup>3+</sup> lasers at the wavelength of  $\lambda = 1060$  nm, pulse duration 10 ns, and pulse repetition frequency 10 Hz. The radiation pulse energy was 0.09 J. Two hot-pressed specimens of HTSC YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> ceramics were used as the targets. The spacing between the substrate and the target was 50 mm. The deposition time was 4 min.



The working chamber pressure was varied from  $10^{-5}$  to  $10^{-2}$  mm Hg. The substrate temperature was varied within 1053–1123 K.

Crystallographic characteristics of the films and substrates were measured at a DRON-6 diffractometer using  $\text{CuK}\alpha$ -radiation. Structural quality of the films was characterized by the angles of misorientation of the  $a$ ,  $b$ , and  $c$  crystallographic axes. The X-ray diffraction analysis revealed that the diffraction patterns from the YBaCuO films on the surface of  $\text{SrTiO}_3$  contained series of reflections (001) up to high orders, evidencing of the crystal lattice orientation along the  $c$ -axis and of the film epitaxial character. The  $a$ - and  $b$ - axes of crystal lattices of the YBaCuO films were found to be parallel to the substrate plane. The specific electrical resistivity  $\rho_{ab}(T)$  in the  $a$  and  $b$  planes, and the critical superconducting parameters of the films were measured using a four-wire method.

The superconducting parameters were determined from the analysis of the dependence of the normalized specific electrical resistivity  $\rho_{ab}(T)/\rho_{ab}(300)$  in the plane  $ab$  of the films formed at different substrate temperatures and the working chamber pressure  $10^{-3}$  mm Hg. The experimental dependences  $\rho_{ab}(T)/\rho_{ab}(300)$  for the films formed at different substrate temperatures are shown at Figure 1. The curve shapes are practically the same. It is evident that apart from a sharp change in the specific electrical resistivity of these films there is a weak temperature dependence  $\rho_{ab}(T)$ .



1- $T_s = 1053$ ; 2 – 1063; 3 – 1073; 4 – 1123; 5 – 1113; 6 – 1083; 7 – 1103; 8 – 1093 K

**Figure 1.** Temperature dependences of the normalized specific electrical resistivity of the films formed at different substrate temperatures  $T_s$ .

In the general case, these curves could be described by a well-known formula that was used in the analysis of the temperature dependence of the specific electrical resistivity of superconducting cuprates in the  $ab$  plane [4]:

$$\rho_{ab} = \frac{\rho_c}{AT \cosh^2 \frac{T_0}{T}}, \quad (1)$$

where  $\rho_c$  – specific electrical resistivity along the  $c$ -axis.

The values of superconducting parameters and  $\rho_{ab}(300)$  of the films obtained from the curves shown in Figure 1 and  $\rho_c(300)$  calculated by the formula (1) are listed in Table 1. When calculating  $A$  parameter, the experimental results on oxygen stoichiometry ( $7-x$ ) were used. The critical temperature

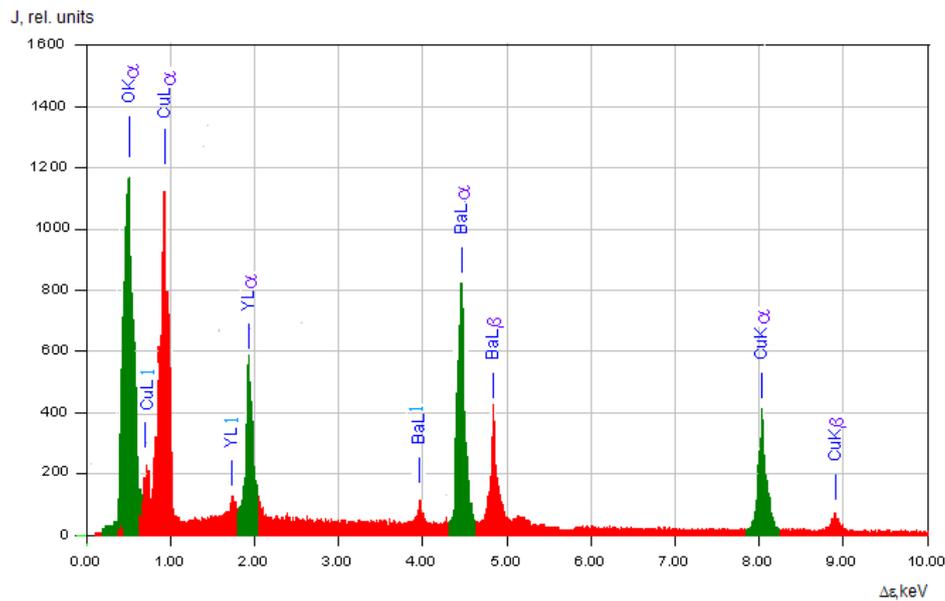
of the superconducting transition  $T_c$  is determined by the level of  $0.5\rho_{ab}(T)$ , and the width of the superconducting transition  $\Delta T_c$  – by the difference of the levels  $0.9\rho_{ab}(T)$  and  $0.1\rho_{ab}(T)$ .

**Table 1.** Values of superconducting parameters of YBaCuO films.

$T_s$ , K	$\rho_{ab}(300)$ , m $\Omega$ ·cm	$\rho_c(300)$ , m $\Omega$ ·cm	$T_c$ , K	$\Delta T_c$ , K
1053	0,259	7,771	88,0	4,0
1063	0,300	9,000	88,7	2,6
1073	0,157	4,553	89,0	2,0
1083	0,190	5,130	90,7	1,7
1093	0,230	4,830	92,0	1,8
1103	0,260	6,240	91,2	2,3
1113	0,280	7,560	90,6	3,0
1123	0,330	9,240	89,5	3,5

It follows from Table 1 that for all films there is high-temperature superconductivity at  $T_c \geq 88$  K. The films with  $T_s=1093$  and  $1083$  K demonstrate a significantly sharp transition into superconducting state, while the samples with  $T_s=1053$ ,  $1113$  and  $1123$  K show a comparatively gradual transition into superconducting state. The lower substrate temperature bound, where the YBaCuO film transits into superconducting state at the temperature  $88$  K, corresponds to the substrate temperature about  $1053$  K. The upper bound, at which formation of the YBaCuO film is still possible, corresponds to the substrate temperature about  $1123$  K. For YBaCuO films in the substrate temperature interval  $1083$ – $1103$  K, the superconducting parameters slightly vary. It should be noted that there is a narrow substrate temperature interval at which optimal superconducting parameters are achieved for YBaCuO films. The different character of variation of YBaCuO films properties is worth mentioning, when the films are formed at substrate temperatures decreasing and increasing with respect to their optimal values.

The calculation of oxygen stoichiometry ( $7-x$ ) of the investigated films was based on microanalysis of their elemental composition using a special PHI-RHO-Z code via a mathematical processing of the characteristic of X-ray energy dispersion spectra. The microstructural analysis and the measurement of energy dispersive spectra from the YBaCuO films were carried out on a JEOL JSM-5910 scanning electron microscope (SEM). Figure 2 shows the characteristic of X-ray energy dispersive spectra from elemental components of the films with  $T_c=89$  K and  $\Delta T_c=2.0$  K. The peaks corresponding to all elemental components of the films are evident in these spectra. The probe electrons energy is  $20$  keV, the probe current is  $0.1$  nA, the duration of measurements is  $50$  s. The obtained peaks are:  $OK_\alpha$ ,  $YL_\alpha$ ,  $YL1$ ,  $BaL_\alpha$ ,  $BaL1$ ,  $BaL_\beta$ ,  $CuL_\alpha$ ,  $CuL1$ ,  $CuK_\alpha$ , and  $CuK_\beta$ . According to the dipole selection rules [5], the peaks  $OK_\alpha$ ,  $CuK_\alpha$  result from an electron transition  $2p_{3/2} \rightarrow 1s_{1/2}$  and correspond mainly to the valent p-electrons of oxygen and copper atoms;  $YL_\alpha$ ,  $BaL_\alpha$ ,  $CuL_\alpha - 3d_{5/2} \rightarrow 2p_{3/2}$  result from small contributions of s-electrons into the electron intensity and bear information on d-electrons of the atoms of yttrium, barium, and copper;  $BaL_\beta - 3d_{3/2} \rightarrow 2p_{1/2}$ ;  $CuK_\beta - 3p_{3/2} \rightarrow 1s^{1/2}$ ;  $YL1$ ,  $BaL1$ ,  $CuL1 - 3s_{1/2} \rightarrow 2p_{3/2}$  represent the 3s-electrons of the atoms of yttrium, barium, and copper, which do not participate in the formation of chemical bonding.

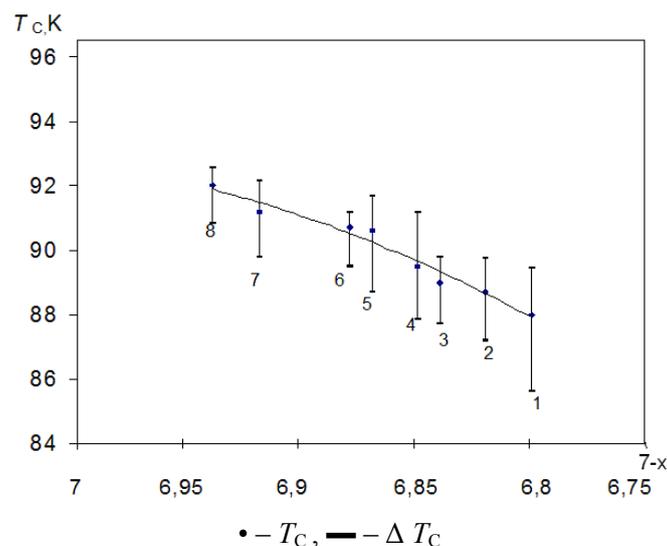


**Figure 2.** Characteristic X-ray energy dispersive spectra from an YBaCuO film at  $T_c = 89$  K.

A microscopic analysis of the elemental composition was performed using  $OK_\alpha$ ,  $YL_\alpha$ ,  $BaL_\alpha$ , and  $CuL_\alpha$  analytical signals, since the intensity of these signals ( $J$ , rel. units) is higher than that of the remaining peaks. The data presented in Figure 2 were used to determine the X-ray quantum energy: for  $YL_\alpha$   $\Delta\varepsilon = 1.92$  keV, for  $BaL_\alpha$   $\Delta\varepsilon = 4.46$  keV, for  $CuL_\alpha$   $\Delta\varepsilon = 0.930$  keV, for  $OK_\alpha$   $\Delta\varepsilon = 0.525$  keV.

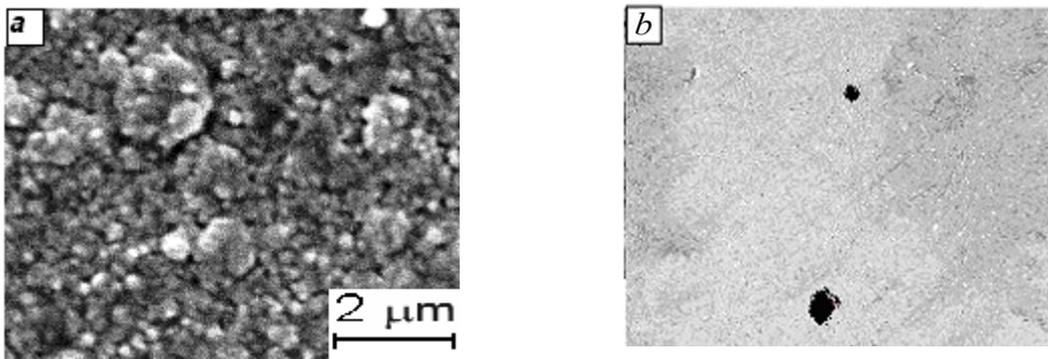
Based on the performed calculations using the data of the energy dispersive spectra, it was found out that within the selected substrate temperature interval the oxygen stoichiometry in YBaCuO films lies within the range 6.8–6.94. At substrate temperature about  $T_s = 1093$  K there is a maximum concentration of oxygen in the film [6].

The established dependences of the critical temperature and the width of the superconducting transition on the oxygen stoichiometry  $7-x$  based on the Figure 1 and the Table 1 are shown in Figure 3.



**Figure 3.** Dependences of superconducting parameters of the films on oxygen stoichiometry

At the oxygen stoichiometry 6.94, the film has a maximum  $T_c$ , while at 6.8 –  $T_c$  is minimal. The microstructure of the YBaCuO film with  $T_c = 88$  K and  $\Delta T_c = 4$  K formed at  $T_s = 1053$  K possesses a pronounced granular structure with a predominance of spherical grains (Figure 4, a). Neither regular patterns in grain arrangement nor predominant direction in their orientation are observed. For the films with  $T_c = 92$  K and  $\Delta T_c = 1.8$  K formed at  $T_s = 1093$  K a higher microstructure density, smoothness and uniformity are observed compared to those films with  $T_c = 88$  K. There are spherical regularly shaped microdrops on the surface (Figure 4, b). The works [7, 8] showed that high values of the superconducting transition critical temperature ( $T_c = 92$  K) and optimal values of  $\Delta T_c$  result from the uniformity and dense low-defect microstructure of the YBaCuO films.



a –  $T_c = 88$  K,  $\Delta T_c = 4$  K

b –  $T_c = 92$  K,  $\Delta T_c = 1,8$  K

**Figure 4.** Microstructure of the films with different superconducting parameters

The observed dependence of the film structure on the deposition temperature could be interpreted in the following way. Structural formation of YBaCuO films occurs directly in the process of deposition. As the material is supplied onto the substrate, there is the formation and growth of crystal nuclei with maximum growth rate anisotropy. Due to migration of the adsorbed particles, there is a physical contact between the granules. If the interaction between the granules is stronger than that between the granules and the substrate, the crystallites are aggregated into big clusters. This process would be enhanced with the temperature increase.

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