

EFFECT OF OXYGEN STOICHIOMETRY AND MICROSTRUCTURE ON SUPERCONDUCTING PROPERTIES OF YBaCuO FILMS

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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.

A major material employed in the present-day cryoelectronics is high-temperature superconductor (HTSC) $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBaCuO) whose films are formed on a variety of dielectric substrates [1]. The investigation of the relationship between microstructure and superconducting characteristics of YBaCuO films is appealing not only from scientific standpoint but also in terms of their practical applications. It is quite clear that the main superconducting properties of the films – critical temperature T_c , width of superconducting transition ΔT_c , and density of critical current J_c – depend on how ideal the microstructure of the resulting films is. This is mainly controlled by the force of interaction of the Abrikosov vortices with crystal defects, i.e., the pinning force – locking of the vortices onto microstructure imperfections [2, 3]. Planar defects of microstructure of YBaCuO films 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 ΔT_c of the superconducting transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are functions of the oxygen stoichiometry ($7-x$). 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.

In this work, we address the relationship between structural properties and superconducting characteristics of YBaCuO films formed by laser ablation on a single-crystal SrTiO_3 (100) substrate.

In order to deposit these films, we used a universal laser setup that consisted of two lasers, a universal vacuum station, a system of laser emission control, and a system of substrate temperature T_s control. The films were deposited by evaporation of the targets by two crossed YAG-Nd lasers at the wavelength $\lambda = 1060$ nm, pulse duration 10 ns, and pulse repetition frequency 10 Hz. The radiation pulse energy was 0.09 J. The targets used were hot-pressed specimens of HTSC $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics. 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} millimeter of mercury. The substrate temperature was varied within 1053–1123 K.

Crystallographic characteristics of the films and substrates were measured in a DRON-6 diffractometer using $\text{CuK}\alpha$ -radiation. Structural quality of the films was characterized by the angles of misorientation of the crystallographic axes a , b , and c . The X-ray diffraction analysis revealed that the diffraction patterns from the YBaCuO films on the surface of 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 crystal lattices of the YBaCuO films were found to be parallel to the substrate plane. The specific electrical resistivity in the planes a and b , $\rho_{ab}(T)$, 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} millimeter mercury. The experimental dependences $\rho_{ab}(T)/\rho_{ab}(300)$ for the films formed at different

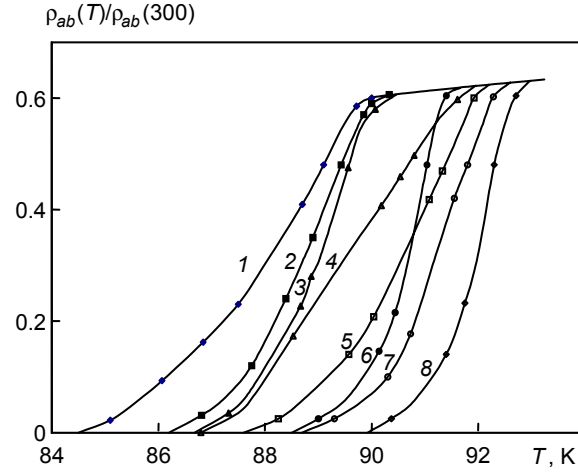


Fig. 1. Temperature dependences of the normalized specific electrical resistivity of the films formed at different substrate temperatures T_s , K: 1053 (curve 1), 1063 (curve 2), 1073 (curve 3), 1123 (curve 4), 1113 (curve 5), 1083 (curve 6), 1103 (curve 7), and 1093 (curve 8).

substrate temperatures are given in Fig. 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 $\rho_{ab}(T)$.

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 ρ_c is the specific electrical resistivity along the c -axis. Systematic experimental studies of single crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at $(7-x) < 7$ demonstrate that the resistivity ρ_{ab} exhibits “metallic” behavior, while that along the c -axis demonstrates “nonmetallic” behavior. Constant T_0 for average concentrations of oxygen remains largely independent of oxygen concentration $T_0 \approx 548$ K. At the same time, constant A changes with oxygen concentration as

$$A = a[(7-x) - b]^{-m}. \quad (2)$$

The optimal values of the constants are as follows: $a = 0.073$, $b = 6.34$, and $m = 1.62$. We may, therefore, assume that the mechanism of high-temperature superconductivity in YBaCuO films could be explained according to the theory based on the model of resonant electron tunneling [4].

The values of superconducting parameters and $\rho_{ab}(300)$ of the films obtained from the curves shown in Fig. 1 and $\rho_c(300)$ calculated by the formula in Eq. (1) are listed in Table 1. When calculating parameter A , we used the data from Table 2 that lists the experimental results on oxygen stoichiometry $(7-x)$. 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 ΔT_c – by the difference of the levels $0.9\rho_{ab}(T)$ and $0.1\rho_{ab}(T)$.

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 specimens 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 1053 K. The upper bound, at which formation of a YBaCuO -film is still possible, corresponds to the substrate temperature 1123 K. For YBaCuO -films in the substrate temperature interval 1083–1103 K, the superconducting

TABLE 1. Values of Superconducting Parameters of YBaCuO Films Formed at Different Substrate Temperatures T_s

T_s , K	$\rho_{ab}(300)$, m Ω ·cm	$\rho_c(300)$, m Ω ·cm	T_c , K	ΔT_c , K
1053	0.259	7.771	88.0	4.0
1063	0.300	9.0	88.7	2.6
1073	0.157	4.553	89.0	2.0
1083	0.190	5.13	90.7	1.7
1093	0.230	4.83	92.0	1.8
1103	0.260	6.24	91.2	2.3
1113	0.280	7.56	90.6	3.0
1123	0.330	9.24	89.5	3.5

TABLE 2. Data From Quantitative Microanalysis

T_s , K	Oxygen concentration, at. %	$7-x$	Chemical formula according to analytical data
1053	52.169	6.80	YBa ₂ Cu _{2.97} O _{6.80}
1063	52.799	6.82	YBa ₂ Cu _{2.99} O _{6.82}
1073	52.850	6.84	YBa ₂ Cu _{2.99} O _{6.84}
1083	53.213	6.88	YBa ₂ Cu _{2.99} O _{6.88}
1093	53.432	6.94	YBa ₂ Cu _{2.99} O _{6.94}
1103	53.384	6.92	YBa ₂ Cu _{2.98} O _{6.92}
1113	53.161	6.87	YBa ₂ Cu _{2.98} O _{6.87}
1123	52.980	6.85	YBa ₂ Cu _{2.98} O _{6.85}

parameters vary but slightly. 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 properties of YBaCuO-films is worth mentioning, when the films are formed at substrate temperatures decreasing and increasing with respect to their optimal values.

The reasons for the considerable effect of the substrate temperature on superconducting characteristics of YBaCuO-films might be accounted for by a direct influence of the deposition conditions in the course of formation of superconducting properties on their oxygen stoichiometry and microstructure.

The calculation of oxygen stoichiometry ($7-x$) of the investigated films was carried out on the basis of microanalysis of their elemental composition using a special PHI-RHO-Z code via a mathematical processing of the characteristic X-ray energy dispersion spectra. In the microstructural analysis and for the measurement of energy dispersive spectra from the YBaCuO-films, use was made of a JEOL JSM-5910 scanning electron microscope (SEM). Figure 2 shows the characteristic 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 electrical probe energy is 20 keV, the current is 0.1 nA, and the duration of measurements is 50 s. The peaks obtained are: OK_α , YL_α , $YL1$, BaL_α , $BaL1$, BaL_β , CuL_α , $CuL1$, CuK_α , and CuK_β . According to the dipole selection rules [5], the peaks OK_α , CuK_α 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_α , BaL_α , $CuL_\alpha - 3d_{5/2} \rightarrow 2p_{3/2}$ 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.

A microscopic analysis of the elemental composition was performed using analytical signals from OK_α , YL_α , BaL_α , and CuL_α , since the intensity of these signals (I , rel. units) is higher than that of the remaining peaks. The data presented in

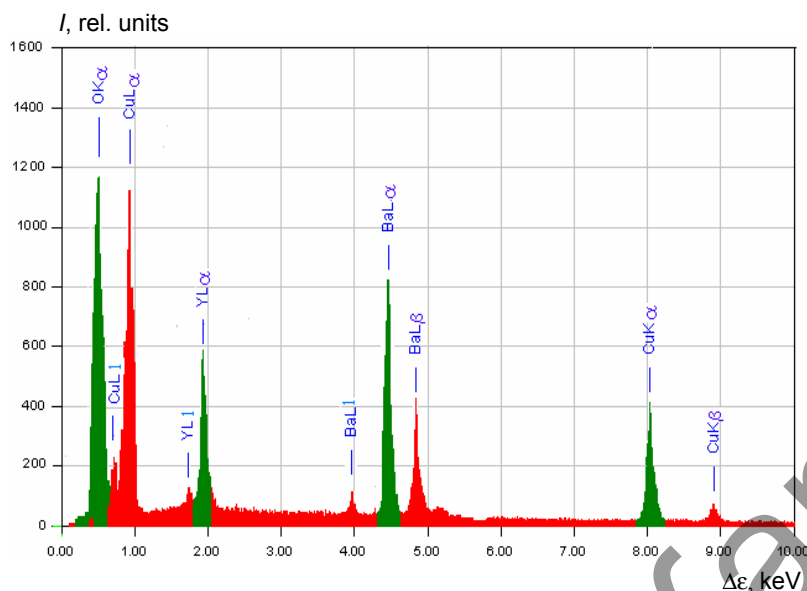


Fig. 2. Characteristic X-ray energy dispersive spectra from an YBaCuO film at $T = 89$ K.

Fig. 2 were used to determine the X-ray quanta energy: $YL_{\alpha} - \Delta\epsilon = 1.92$ keV, $BaL_{\alpha} - \Delta\epsilon = 4.46$ keV, $CuL_{\alpha} - \Delta\epsilon = 0.930$ keV, and $OK_{\alpha} - \Delta\epsilon = 0.525$ keV. The position of the CuL_{α} peak differs from that in the spectrum of CuO insignificantly, since the charge state of the copper atoms in the specimens under study is generally the same as that in CuO.

Based on the calculations performed using the data of the energy dispersive spectra, we have found out that within the selected substrate temperature interval the oxygen stoichiometry in YBaCuO-films lies within the range 6.8–6.94. The results of the microanalysis demonstrate that the concentration of the atoms of yttrium, barium and copper does not vary under variation of T_s . The data on atomic concentration of oxygen (in at. %) and oxygen stoichiometry, and also the respective chemical formulas are given in Table 2. The values of oxygen atom concentrations are averaged with respect to several tests. It is evident that at $T_s = 1093$ K there is a maximum concentration of oxygen in the film. Above and below this substrate temperature, oxygen concentration is decreased. This might be due to oxygen desorption at high substrate temperatures. The standard relative deviation of determining oxygen stoichiometry of the films lies in the range $S_r = 0.0008$ – 0.0009 . The calculated value of the confidence interval of determining oxygen stoichiometry was found to be equal to $\epsilon_p = \pm(0.005$ – $0.006)$ for the confidence probability $p = 0.95$.

The investigations carried out using the methods of high-temperature X-ray and neutron diffraction, thermosorptive MS, thermography, and thermogravimetry demonstrated that at $7 \geq (7-x) \geq (6.4$ – $6.5)$ $YBa_2Cu_3O_{7-x}$ are characterized by a rhombic symmetry and transit into superconducting state at $T_c \approx 70$ – 95 K [5]. At $(6.4$ – $6.5) \geq 7-x \geq 6$, this compound exhibits tetragonal symmetry and possesses superconducting properties at low critical superconducting parameters with respect to the compound with rhombic symmetry [6]. This is indicative of the fact that the rhombic phase predominates in the films formed, since for these films the oxygen stoichiometry lies in the interval 6.8–6.94. The value of the lattice parameter c in the best quality specimens reached ~ 11.7 Å, corresponding to the oxygen stoichiometry 6.94.

The dependences of the critical temperature and the width of the superconducting transition on the oxygen stoichiometry $7-x$ based on the data of Fig. 1 and Table 2 are depicted in Fig. 3.

At the oxygen stoichiometry 6.94, the film has a maximum T_c , while at 6.8 – it is maximal. The films with high T_c have the lattice parameter c close to 11.7 Å. As c is increased, the value of T_c is gradually decreasing. The maximum values of superconducting parameters correspond to the minimum values of the angles of misorientation of the c -axis of the films with respect to the substrate plane $\Delta\theta$ and the a and b – axes in the substrate plane $\Delta\gamma$. The dependences of T_c on oxygen stoichiometry for obtained for the YBaCuO-films do not contradict the well-known data on the dependence of T_c on $7-x$ for the ceramic $YBa_2Cu_3O_{7-x}$ specimens.

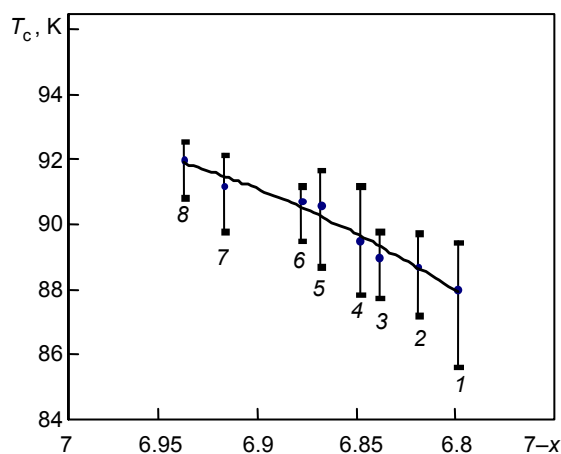


Fig. 3. Dependences of superconducting parameters of the films on oxygen stoichiometry $7-x$: T_c (●) and ΔT_c (■).

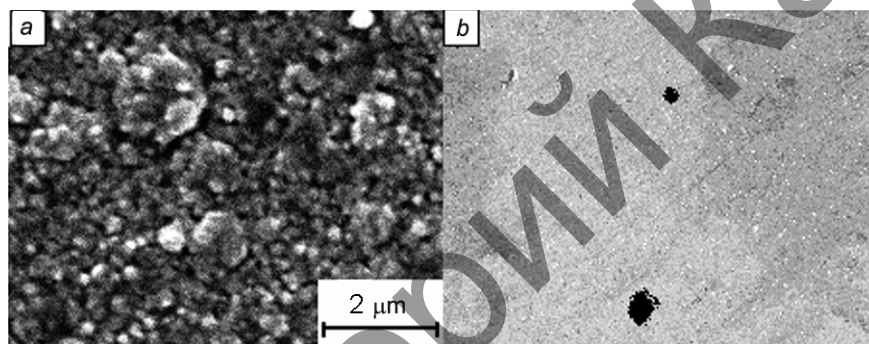


Fig. 4. Microstructure of the films with different superconducting parameters: $T_c = 88$ K, $\Delta T_c = 4$ K (a) and $T_c = 92$ K, $\Delta T_c = 1.8$ K (b).

A correlation between the unit cell parameters, the content of oxygen and the temperature of transition of the initial ceramic into superconducting state could possible explain the nature of the effect of oxygen stoichiometry of the films on their superconducting properties. In a superconducting phase at $7-x \approx 7$, the interaction between the neighboring layers with strong Cu–O interaction occurs through a chain of flat squares of CuO_4 . A decrease in $7-x$ results in destruction of these chains and gradual decrease of T_c . At $7-x = 6$, the chain is totally absent. There are additional oxygen vacancies appearing in the Cu1 plane, and there is a change in the coordination neighborhood of Cu1 and Ba atoms. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic at $7-x = 6$ is a semiconductor in which no transition into superconducting state is observed until helium temperatures [7].

The microstructure of a YBaCuO film with $T_c = 88$ K and $\Delta T_c = 4$ K formed at $T_s = 1053$ K possesses a pronounced granulated structure with a predominance of spherical grains (Fig. 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 we observed higher microstructure density, smoothness and uniformity than those in a film with $T_c = 88$ K. On the surface there are spherical regularly shaped microdrops (Fig. 4, b). In [8, 9], it was shown that high values of the critical temperature of the superconducting transition ($T_c = 92$ K) and optimal values of ΔT_c result from the uniformity and dense low-defect microstructure of the YBaCuO films.

The observed dependence of the film structure on the deposition temperature could be interpreted in the following way. Structure of the YBaCuO films is formed immediately in the course of deposition. As the material is supplied onto the substrate, there is a growth of crystal nuclei with a maximum growth rate anisotropy. Due to migration of the adsorbed

particles, there is a physical contact of the granules with each other. If the interaction between the granules is stronger than that between the granules and the substrate, the crystallites are aggregated into big clusters (liquid-like coalescence). This process would be enhanced with the increase in temperature.

The consideration of the experimentally observed features of the effect of microstructure on superconducting properties of the films relies on a phenomenological representation of these films as a set of superconducting granules. The reasons explaining the effect of the microstructure character on T_c and ΔT_c stem from the sensitivity of superconducting properties to different types of defects and the importance of the role of weakly bound grain interlayers (Josephson's contacts) on the critical current value. It is likely that superconducting state is formed inside the grains at the temperatures below T_c . In the case of a non-uniform granular structure, the grains are coupled by a weak Josephson force. As soon as a smooth uniform structure is formed, the Josephson contacts couple the superconducting grains into a single current-conducting system, in which superconducting state is maintained on a large area of the film at $T_c \geq 89$ K. To sum up, it should be noted that minimization of the weak forces, combination of individual superconducting grains, and decrease in the grain misorientation angle in the ab plane to a zero value, which ensures maximum values of T_c and J_c , have been achieved by specially selecting the conditions of deposition.

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