Diagnostics of target inhomogeneity and influence of YBCO target oxygen content on properties of HTSC 2G samples fabricated by PLD technique

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Abstract. The pulsed laser deposition (PLD) targets used for HTSC 2G fabrication should be uniform and chemically suitable to make long tapes with reproducible critical properties. We investigated inner density distribution of flat YBCO targets using non-destructive neutron introscopy and tomography techniques. The methods are based on absorption of monochromatic neutron beam which is going through the specimen. In first set of targets we measured variance of material density (up to 10-25%) with maxima density located in central layer of the target body. After updating of target fabrication technology no significant density inhomogeneity were detected. The dependence of critical current of superconducting films with thickness of 300 nm deposited on sapphire substrate with appropriate buffer layers using PLD YBCO targets with various oxygen content was also investigated. Oxygen index of YBCO targets vary from 6.12 to 6.85. No significant influence of target oxygen index on critical current density of fabricated films was detected.

1. Introduction
The method of Pulsed Laser Dispersion (PLD) allows manufacturing of long length second generation (2G) HTS conductors with extremely high current-carrying capacity. The main advantage of the PLD method is stoichiometric transfer of a material from the target to the substrate that defines high requirements to quality of the targets to be sprayed. The target for PLD has to be uniform by density to keep conditions of laser sputter plume formation for a long time and to provide fabrication of long tapes with reproducible critical characteristics. In this paper the application of nondestructive methods of a neutron radiation introscopy and tomography for testing of uniformity of PLD target density.

Besides, practical interest is the influence of an oxygen index of PLD target on properties of the fabricated coating. The influence of number of PLD target parameters such as grain size, density, cationic stoichiometry (Y, Ba and Cu), composition and percentage of the impurities (acting as the pinning centers) on critical characteristics of fabricated HTSC coatings was under intensive investigations [1-5]. However influence of an oxygen index of the target on characteristics of formed epitaxial layers remains insufficiently studied. It is well known that critical characteristics of both bulk HTSC and films depend on the content of oxygen (index) in the unit cell of YBa₂Cu₃Oₓ [6, 7].
YBCO the superconducting orthorhombic phase with a critical temperature of about 90 K exists at 6.8<x<7.0, the phase with T_C about 60 K corresponds to 6.6<x<6.8 but when oxygen concentration x<6.5 there is a transition to a tetragonal not superconducting phase. Possibility of formation of coatings with high value of critical temperature from a target with the low oxygen content of x=6.55 was demonstrated earlier [8].

It is credible that during long-duration PLD process the temperature of the target surface could reach up to several hundred centigrade due to heat radiation from substrate. As the deposition process of all epitaxial layers (buffer and superconducting) of HTSC tapes is carried out in high vacuum or in inert gas atmosphere or in the oxygen environment there can be a considerable variations of HTSC target oxygen index due to diffusion of oxygen from/to the target. So the influence of such target surface oxygen index variation on critical current of fabricated epitaxial HTSC films is very important.

2. PLD target preparation

All targets were fabricated in Bochvar Institute. The basic manufacturing techniques are earlier described in paper [9]. Briefly, the technology includes preparation of the mix of nitrate solutions of yttrium and copper and barium nitrite solution; carrying out joint sedimentation of oxalates; drying and processing of an oxalate deposits; pyrolysis of oxalate powder; powder processing after pyrolysis; pressing of targets, heat treatment of targets.

The first set of targets (denoted below as #216, 217, 259, 261, 262, 264) were made with dry powder pressing technique without using of binding substance. Diameter of these targets was about 20 mm. Mean powder size was about 10 microns. Pressing power varies from 0.5 to 5 t/cm^2. The average density of targets was from 5.3 to 5.95 g/cm^3.

The updated target fabrication technology includes powder pressing technique with specific organic binder. These are targets denoted below as #282, 284, 352-1. Diameter of targets was about 65 mm. Average density of targets was 5.7 – 5.75 g/cm^3.

3. Diagnostics of target inhomogeneity by neutron introscopy and tomography techniques

Advantage of neutron methods of research in comparison with x-ray is large penetration length. The investigations of YBCO PLD targets were carried out on DICTOR installation of neutron research reactor IR-8 in Kurchatov Institute. Determination of macroscopic non-uniformity of the object was done by means of a transmission of a monochromatic thermal neutrons beam through a sample with using of absorbing and diffraction contrast. Output beam from reactor is monochromatic (with wavelength of 1.52 Å) with 40 × 50 mm^2 in size which passes through the sample located on remotely operated motorized goniometer with a vertical axis of rotation. The neutron radiation is registered by the detector consisting of the scintillation screen, the mirror, a lens and remotely operated video camera with Peltye cooled CCD matrix of 4004 × 2671 pixels in size. Spatial resolution of the image is limited by angular divergence of incident neutron beam (about 2.5 deg.) and is about 400 microns on the sample. The sample image on the detector was formed mainly due to absorbing contrast that allows to visualize distribution of absorbing ability and substance density. In the presence of large crystalline grains there can be an additional diffraction contrast Program-controlled registration of images by sample rotation round an axis of the goniometer allows to carry out tomographic shooting of a sample in an automatic mode.

In case of a homogeneous uniform sample the distribution of intensity of transferred beam on introscopy image will be uniform. Appearance of contrast areas on the image denote to heterogeneity of a chemical composition and/or local density of the sample.

More detailed information on density distribution in PLD targets can be received by carrying out of full tomographic shooting of targets with small steps of scanning angle of a target regarding to vertical axis. Total duration of shooting of introscopy experiment is about of 2 minutes, in case of a tomography experiment it is about 12 hours. Tomographic shooting consists of 360 projections with a steps of 0.5 deg., and empty beam registration with dark current of the detector. Preprocessing of projections (cleaning of noise, the accounting of a background and non-uniformity of the beam, image
normalization), and also decomposition of virtual cross-section on projections was done by means of ImageJ program macros. Advantage of neutron tomography is that one can easily look on shape of any inhomogeneity areas in the sample and can make any cross-sections inside the sample.

Typical introscopy images and results of interpretation for target #261 are shown on figure 1. Both neutron beam projections (full-face and side-face) allow estimate the measure of inhomogeneity of target. On side-face image the narrow dark area exists in the central part of target. Taking into account intensity of transferred neutron beam (see intensity cross-section profiles marked by 1, 2 and 3 for side-face) we can calculate appropriate variance of density (see corresponding density line for profile 2 which goes through target geometrical center). Maximum variation of density of target is about 26%.

![Figure 1](image1.png)

Figure 1. Introscopy images and results of interpretation for target #261. (a) - full-face image, (b) - side-face image. Right graph shows side-face intensity profiles (1, 2 and 3) and density profile 2.

Calculated maximum variations of density for all PLD targets from first set (dry pressed) are presented in table 1. All targets have area with increased density in the central layer of target body.

| Target # | 262 | 216 | 259 | 261 | 264 |
|---------|-----|-----|-----|-----|-----|
| Maximum density variation (%) | 12  | 10  | 15  | 26  | 15  |

In contrast both tomographic and introscopy images of targets fabricated with organic binder show no variations of density (also in central layer). Figure 2 shows tomographic side-face cross-section of three new targets (#282, 284, 352-1) and of one dry pressed target (#262) for comparison. Maximum density variation for PLD targets does not exceed 3%.

![Figure 2](image2.png)

Figure 2. Tomographic side-face target cross-section. From left to right: #262 (dry pressed, strong inhomogeneity and dense inclusion inside); #282, 284 and 352-1 (all pressed with organic binder, homogenous). Visible concentric circles are artifacts due to tomographic image recovery procedure.

4. Influence of an oxygen index of PLD targets on properties of HTSC coating

We used the YBCO target #217 with diameter of 25 mm and 10 mm in height with average density of 5.95 g/cm³ to fabricate HTSC films. Estimation of the oxygen index variation of the target was carried out by means of x-ray diffraction method (using “oxygen index” vs “c-lattice parameter” dependence [10]) and by changing of the target weight (to within 0.1 mg) after each deposition experiment. Initial oxygen index of the target was x=6.85. All HTSC films with thickness of 300 nm was deposited by
excimer (KrF) laser on single crystal sapphire Al₂O₃ (r-plane) with CeO₂ buffer layer. Substrate temperature was 760°C, oxygen pressure in the chamber was 350 mTorr. Each deposited film had been subjected to post-growth annealing in the oxygen atmosphere with a pressure of 650 Torr during one hour. Critical temperature of films was measured by inductive method. Critical current was measured using the four-probe method on bridges with 1 mm width (77K, self-field). Temperature of the target during process was measured in-situ by thermocouple. It has been found that the target surface temperature reached the maximum of about 500°C in 30 minutes during deposition process.

At the first experiment the influence of target heating on its oxygen index was examined. Target was subjected to warming up within 30 minutes inside deposition chamber, thus temperature of a target reached 500°C. The oxygen index of a target before and after radiation heating has changed from x=6.85 to x=6.60. To simulate influence of buffer layer (CeO₂) growth process on the target oxygen index the vacuum annealing of the target was done with temperature of 500°C during 3 hours. As the result the target oxygen index decreased from x=6.60 to x=6.12. To recover the target oxygen index to an initial x=6.85 the annealing in pure oxygen with a pressure of 600 Torr was carried out with temperature of 500°C during 3 hours. Thus, target oxygen index can vary within 6.85-6.12 during standard deposition process and post-growth annealing.

At the second experiment we deposited HTSC films using the same target but various starting target oxygen index (x=6.12 and x=6.85). Measured oxygen index of both HTSC films was x=6.9 independently on starting target oxygen index. Critical temperature of films was 88-89 K, critical current and critical density were 9.4 A (3.2 MA/cm²) and 10.4 A (3.5 MA/cm²) respectively. Thus, critical characteristics of both samples are almost the same. This can be explained by two factors: 1) oxygen environment in the chamber can re-saturates target with oxygen, and 2) post-growth oxygen annealing of film can re-saturates film with oxygen.

5. Conclusions
In this paper unique nondestructive neutron introscopy and tomography techniques were developed and successfully applied to investigate the PLD target inhomogeneity. The PLD targets fabricated by updated technology with pressing with organic binder are uniform and homogenous as distinct from dry pressed targets which demonstrate up to 25% density variation.

The oxygen index of the PLD target varies in the chamber during deposition process (within limits 6.12-6.85) but the variation does not influence on current-carrying capacity of fabricated HTSC films.

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References
[1] Paturi P, Schlesier K and Huhtinen H 2009 Physica C 469 839
[2] Ijrala M, Huhtinen H, Jha R, Awan V P S and Paturi P 2011 IEEE Transactions on Applied Superconductivity 21 2762
[3] Wee S H, Specht E D, Cantoni C, Zuev Y L, Maroni V, Wong-Ng W, Liu G, Haugan T J and Goyal A 2011 Phys. Rev. B 83 224520
[4] Peurla M, Huhtinen H, Paturi P, Stepanov Yu P, Raittila J and Laiho R 2005 IEEE Transactions on Applied Superconductivity 15 3050
[5] Develos-Bagarinoa K, Yamasaki H, Nakagawa Y and Endo K 2004 Physica C 412–414 1286
[6] Maiti K, Fink J, Jong S, Gorgoi M, Lin C, Raichle M, Hinkov V, Lambacher M, Erb A and Golden M S 2009 Phys. Rev. B 80 165132
[7] Mori Z, Doi T and Hakuraku Y 2010 J. Appl. Phys. 107 023903
[8] Huhtinen H, Paturi P, Lahderanta E and Laiho R 1999 Supercond. Sci. Technol. 12 81
[9] Vorobieva A E, Abdukhanov I M, Rakov D N, Kotova E V and Shikov A K 2012 VANT. Materialovedenie i niev materialy (in Russian) 73 108
[10] Benzia P, Bottizzoa E and Rizzia N 2004 J. of Crystal Growth 269 625