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Investigation of Optically Modified $YBa_2Cu_3O_{7-x}$ Films by Means of X-ray Microanalysis Technique

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This work reports on investigation of remnant oxygen content in optically-modified regions of 0.3-μm-thick $YBa_2Cu_3O_{7-x}$ films, patterned by a laser-writing technique in an inert ambient gas atmosphere at room temperature. A laser-treated region of weak superconductivity with dimensions depending on the size of a laser spot, laser power, and initial content of oxygen is characterized by a lower oxygen content, weaker critical magnetic field, and suppressed both the superconducting critical temperature and the critical current density, as compared to the laser untreated regions. Optically induced (cw-laser, 532-nm-wavelength) heating strongly affects a non-uniform distribution of remnant oxygen content in the film, depending both on the optical power and beam's scanning velocity. A level of oxygen depletion and the size of the oxygen-deficient region have been directly estimated from scanning-electron-microscope spectra with the X-ray microanalysis technique. The results of our measurements were compared with results extracted from electric measurements, assuming a correlation between the remnant oxygen content and the electric transport properties of oxygen-deficient $YBa_2Cu_3O_{7-x}$ films.
Keywords: $YBa_2Cu_3O_{7-x}$ superconducting thin films, oxygen deficient superconductor, remnant oxygen content, light interaction with superconducting material, laser-writing technique.

1. INTRODUCTION

$YBa_2Cu_3O_{7-x}$ (YBCO) superconductor is a material of highly anisotropic orthorhombic crystalline structure [1], which becomes superconducting below a certain critical temperature T_c, critical current density J_c, and critical magnetic field H_{c1}, all dependent on the oxygen content x in the material [2–4]. The oxygen content can be easily changed by means of materials' heating in either oxygen rich atmosphere (with the purpose of x decreasing) or in an inert gas (for increasing x). The YBCO orthorhombic structure gradually varies with x changing in the range from 0 to 1. Decreasing the value of x down to 0.6 makes it possible to obtain a tetragonal, i.e., non-superconducting phase of the material [3]. For even higher x values the material splits into several non-superconducting components like those of Y_2BaCuO_5, Y_2O_3, $BaCO_3$, CuO_2, etc, [5], and becomes an insulator.

Oxygen sensitivity of YBCO can be used for producing novel superconducting micro-devices, in which, e.g., two regions of a superconducting film need to be insulated from each other by a semiconducting/insulating barrier. With this purpose a method of either pulsed- or cw-laser patterning/writing of YBCO films have been developed [6, 7], in parallel to many other methods mainly based on either chemical or physical etching processes. The laser-patterning/writing method is based on light induced local heating of the YBCO thin film, causing a change in its oxygen content in. During the process, oxygen diffuses out or into the hot, laser treated region, depending on the ambient gas atmosphere (oxygen poor vs. oxygen rich). The most important element is that a focused laser beam can produce local heating with the dimension of a laser-modified region mainly depending on the diameter of the beams' spot [7]. It has also been demonstrated in [7] that laser writing of the oxygen-depleted (insulating at cryogenic temperatures) or oxygen-rich (superconducting at cryogenic temperatures) lines in the YBCO thin film is fully reversible. The patterns can be also erased by either a prolonged heating in a furnace, or rewritten by subsequent laser writing in oxygen rich ambient (i.e. in ambient inversed to writing procedure).

In the crystalline lattice of a YBCO superconductor, the oxygen occupies two important sites: the chain site–in the Cu-O chain, and the plane site- in the CuO_2 plane [8]. Oxygen removal means that their atoms leave Cu-O chain sites, causing a decrease of the positive charge in the CuO_2 plane and leading to the increase of the material's resistivity and change in dimensions of the crystalline lattice, due to a modified length of Cu-O bonds. Thus, decreasing the oxygen content x from 0 to 0.6, the crystal a axis shrinks for approximately 0.8 %, while the b- and c-axes expand for 1 % and 0.85 %, respectively [8]. The expansion/shrinking of lattice causes appearance of new defects in the film and the mismatch of the oxygen-depressed material in respect to the oxygen-rich one. Sharpness of the interface between these two phases also decreases and has been estimated to be

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~2 μm for ~(150 – 300)-nm-thick, laser-patterned/written YBCO devices [7].

Using a cw-laser-patterning / writing technique described in detail in [7], we have processed 0.3-μm-thick, 100-μm-long and 50-μm-wide YBCO microbridges with ~5-μm-wide, laser-written oxygen-partially-depleted lines [9]. Due to the presence of partially depressed oxygen lines ($x \sim 0.2$), oriented perpendicularly to the biasing current direction, the resistive transition characteristics of our bridges exhibited a supressed superconducting critical temperature T_c, as compared to the laser untreated regions and a nonlinear stepped-like current-voltage (*I-V*) characteristics at temperatures $T < T_c$ [9].

The stepped-like *I-V* dependence is a hallmark of the coherent motion of Abrikosov vortices moving along oxygen partially supressed line (i. e., in a strictly confined geometry). Such a superconducting constriction can be used as a sensitive device [10] for measuring the strength of either the current or amplitude of the external magnetic field with a precision of a single flux quantum. However, the processes causing the oxygen out-diffusion from the orthorhombic YBCO material and the profile change of the laser-deoxygenated line due to the oxygen redistribution is still not clearly understood.

In the present work, we report on oxygen depletion mechanism during the room-temperature laser-writing procedure of YBCO devices prepared on epitaxial films grown on $LaAlO_3$ substrates. We have investigated laser-writing effect in both oxygen-rich and oxygen-partially-depleted YBCO microbridges by means of scanning-electron-microscope (SEM) with X-ray microanalysis technique. The results of our measurements were compared with the results extracted from electric measurements in [11], assuming a correlation between remnant oxygen content and electric transport properties of oxygen-deficient YBCO films. Our results demonstrate that X-ray microanalysis technique can serve as a method for a direct estimation of approximate dimensions of oxygen-deficient regions and evaluation of remnant oxygen content in this region of the film.

2. SAMPLES AND EXPERIMENTAL SETUP

Our 0.3-μm-thick, 100-μm-long, and 50-μm-wide superconducting microbridges were laser-patterned from YBCO epitaxial films. Films were grown by means of metaloorganic chemical vapour deposition (MOCVD) technique on crystalline $LaAlO_3$ substrates at substrate temperature of 830 ºC, followed by post-annealing at 350 ºC in pure oxygen ambient to achieve fully oxygenated YBCO (i. e., with $x \sim 0$). More details of the MOCVD method and technology of thin YBCO films are given in [12].

The X-ray diffraction pole figures and θ–2θ scans demonstrated that our superconducting films had the crystalline *c*-axis oriented perpendicularly to the substrate. The YBCO films were characterised by critical current density $J_c = (3 – 6)$ MA/cm^2 at $T = 78$ K, and $T_c = 92$ K.

The films were laser-patterned (LP) at room temperature using a 532-nm wavelength beam, generated by an Ar-ion, cw-laser, and focused by optical lenses (see Fig. 1) into a light spot's diameter of ~5 μm. Ready for patterning YBCO films were attached perpendicularly to the laser beam's direction on a computer-controlled *X–Y* translation stage and kept in a nitrogen gas ambient.

The laser power of 2.0 W ÷ 2.3 W and a scanning speed of 5 μm/s of the *X–Y* stage ensure full deoxygenation (i. e. $x > 0.6$) of the laser illuminated film's areas, converting them into an insulator [11]. In this way, the YBCO film has been patterned into a set of six microbridges each with large contact areas for the 4-probe electric measurements (Fig. 1).

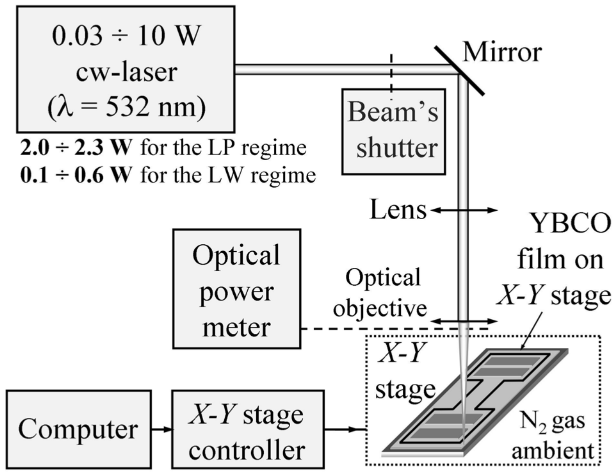

Fig. 1. The setup for LP and LW of the YBCO thin-film devices in a nitrogen gas ambient

The lower illumination power, ranging from 0.1 W to 0.6 W from the cw-laser and a 50 μm/s velocity of the *X–Y* stage were used for the laser-writing (LW) procedure [7] of 5-μm-wide partially deoxygenated (i. e., $x \sim 0.2$) lines in the YBCO film keeping the film in a nitrogen gas ambient. The laser beam's size defined the width of partially deoxygenated region in the film. In this way, we obtained a set of six identical microbridges, five consisted either one or two LW lines, while one sample was left as a pristine device for a reference purposes.

After the LW procedures the film's illuminated areas exhibited J_c, T_c, and the first critical magnetic field H_{c1} comparatively lower than those of the sample without the LW lines [13].

Four silver electrodes (Fig. 1) were thermally deposited in low vacuum for each device by means of 0.1-μm-thick Ag layer evaporation through a special mask. After Ag deposition, the devices were additionally annealed at temperature 300 ºC in oxygen ambient for 1 hour. The chosen temperature for annealing was too low for oxygen redistribution in the superconducting sample, but high enough for silver diffusion into the film. Direct measurements of the Ag/YBCO contact resistance showed that it is practically negligible.

A remnant content of oxygen in laser-modified YBCO films has been extracted from electric measurements in [11], assuming a correlation between the oxygen content and electric transport properties of oxygen-deficient films. Independently, a profile of the oxygen content has been measured down to the film's depth of 100 nm at room temperature by means of SEM with X-ray microanalysis technique. These and other results of measurements are presented and discussed below.

3. RESULTS AND DISCUSSION

A micrograph and a magneto-optical measurement image of a LP YBCO film are shown in Fig. 2. The optical image of two microbridges with one of large areas for Ag contact pads has been taken at room temperature by means of illumination the device by a visible light from the substrate side. Therefore, bright areas in the image correspond to transparent (i. e., insulating) material which is decomposed down to $x > 0.6$ [11].

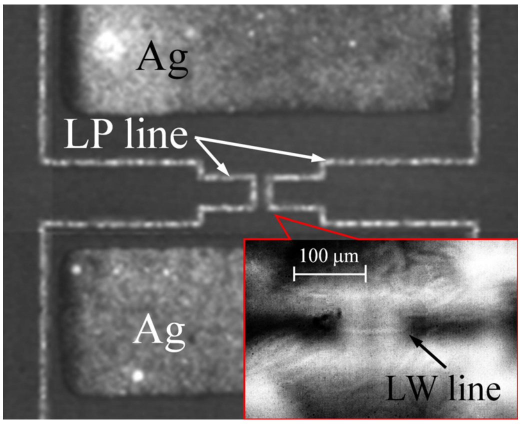

Fig. 2. A view of a YBCO thin film with LP (bright) insulating lines. Bright areas correspond to higher transparency of the light when a sample is illuminated from the bottom side. Inset: magneto-optical image of the penetration of the 280 G magnetic field into the superconducting device containing a single LW line. Bright areas in the inset correspond to higher intensity of a local magnetic field

Inset of Fig. 2 shows a magneto-optical image of the YBCO film in the 280 G external magnetic field. The magnetic field penetrates along the device's edges (insulating lines) and along the LW line of week superconductivity in the microbridge center. Bright areas correspond to higher intensity of a penetrated magnetic field.

The magneto-optical image in Fig. 2 confirms that magnetic flux penetrates first in the areas of weak superconductivity, while the remaining area of the device or contact pads are practically free of flux penetration. This let us to conclude that LW procedure resulted in partially deoxygenation of YBCO material with considerably decreased parameter H_{c1}. It means that the oxygen content in the LW-region of the YBCO film can be controlled during the LW procedure by varying the incident light power from the cw-laser.

Figure 3 demonstrates a profile of relative residual amount of oxygen vs. distance in our YBCO microbridges without (curve #1) and with the single LW region produced at room temperature by the laser illumination power of 0.4 W (curve #2) and 0.6 W (curve #3), measured by means of the X-ray microanalysis technique. For the better observation, the traces $x \sim 0$ and $x > 0.6$ are artificially shifted from the zero position. All three superconducting bridges have been patterned in the same YBCO film, which had the same initial oxygen content. The arrow in Fig. 3 shows an approximate coordinate of the laser beam's center location on the YBCO bridge surface during the LW procedure.

We note in Fig. 3 that, due to the channeling of oxygen diffusion along random distributed film's defects, profiles of the LW lines are somewhat asymmetric with the most pronounced effect seen in curve #3.

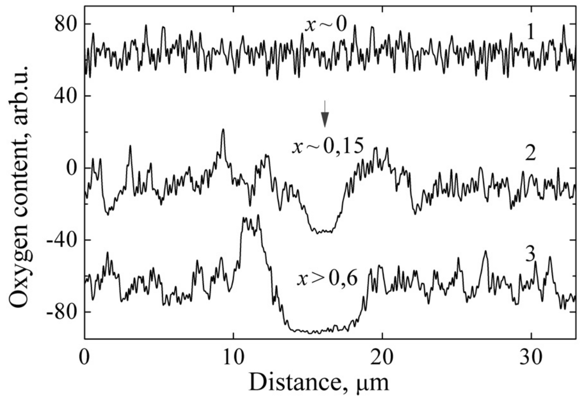

Fig. 3. The residual amount of oxygen vs. distance in three YBCO microbridges: without the LW region (curve #1), and the LW channel generated with the light power of 0.4 W and 0.6 W, (curve #2 and #3, respectively. For clarity, curves #1 and *#3* are artificially shifted from zero position. A residual oxygen content *x* listed in the figure has been extracted from experimental results in [11]. The arrow in figure shows a approximate coordinate of the laser beam's center located on the bridges surface during the LW procedure

Presence of an LW region in the YBCO film can be also determined from the film's electric properties. Figure 4 demonstrates the resistivity $\rho_{a\text{-}b}$, measured along *a-b* plane of the crystalline lattice, vs. temperature for YBCO microbridges before and after the LW process at different incident powers of light from the cw-laser.

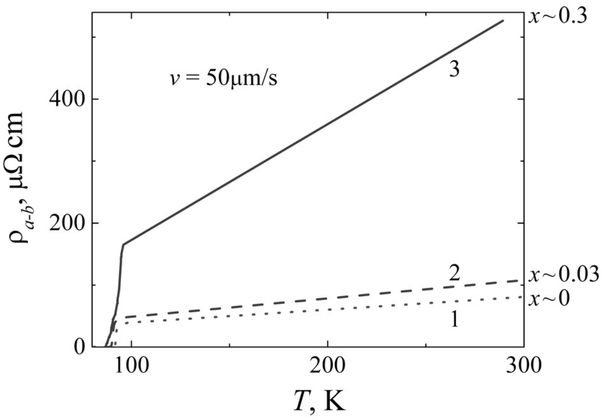

Fig. 4. Resistivity $\rho_{a\text{-}b}$ vs. temperature dependences of YBCO devices containing an LW line produced using laser power of 0.22 W (curve #2) and 0.41 W (curve #3). Curve #1 is the reference, untreated device. Oxygen content *x* in the LW region (see the right *y* axis) has been extracted from [11], assuming a correlation between remnant oxygen content in defects/defect-free YBCO material and electric transport properties of oxygen-deficient YBCO films

After the LW procedure, the room temperature $\rho_{a\text{-}b}$ of the device increased from 105 μΩcm to 530 μΩcm at laser's power 0.22 W (curve #2) and 0.41 W (curve #3), respectively. The increase in $\rho_{a\text{-}b}$ is associated with the decrease of oxygen content along the *b*-axis Cu-O chains of the YBCO crystalline structure, as well as with oxygen depletion in structural defects of the film [14]. The oxygen content x in the LW region (see the right axis in Fig. 4), extracted from [11], shows a direct correlation between the remnant oxygen in defects of the crystalline structure of the YBCO film.

The room temperature $\rho_{a\text{-}b}(300\text{ K})$ and shape of the $\rho_{a\text{-}b}(T)$ dependence in the LW region depend on the initial oxygen content (i. e., the oxygen content before LW procedures) in the YBCO film. These results, measured for the YBCO devices with initial oxygen content $x \sim 0$ (curve #1) and $x \sim 0.1$ (curve #2), are presented in Fig. 5.

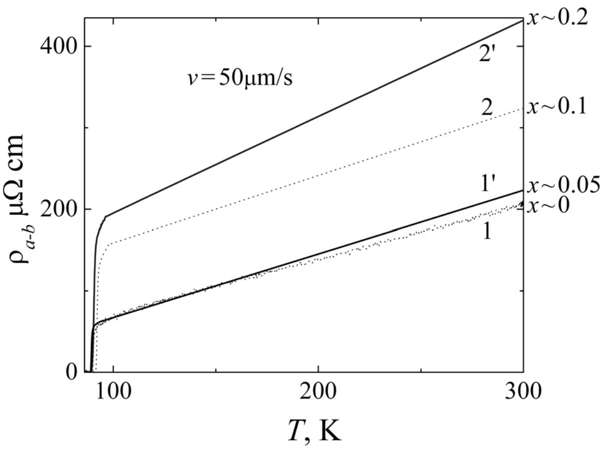

Fig. 5. The electric resistivity $\rho_{a\text{-}b}$ vs. temperature dependences of two YBCO superconducting microbridges with the different initial content of oxygen: $x \sim 0$ (curve #1) and $x \sim 0.1$ (curve #2) and after the LW procedure with the laser power of 0.22 W: curves #1' and #2', respectively. The values of oxygen content x have been extracted from [11]

After the LW procedure at constant illumination power of 0.22 W, $\rho_{a\text{-}b}$ increased from 210 μΩ cm (curve #1) to 225 μΩ cm (curve 1') and from 325 μΩ cm (curve #2) to 430 μΩ cm (curve 2') in both microbridges, respectively. All $\rho_{a\text{-}b}(T)$ dependences have been measured at the biasing current 0.1 mA. The approximate values of oxygen content x in Fig. 5 have been extracted from results in [11].

Knowing the light absorption coefficient of the YBCO material [15], illumination power of 0.22 W, and spot translation velocity of 50 μm/s we have estimated that the temperature of the laser-illuminated paths did not exceed 500 °C during the LW process. At temperature 500 °C, the activation energy of atomic oxygen diffusion in the direction parallel to the *a-b* plane is an order of magnitude higher than that in the *c*-axis direction [16]. Therefore, the most pronounced oxygen depletion is expected to occur at the film surface. Two-dimensional structural growth defects may, however, channel the diffusing oxygen along their directions [14] and the LW processing is likely to result in stronger deoxygenation at the boundaries of the two-dimensional defects. The latter leads to formation of high-resistivity regions that are responsible for the shape of the whole $\rho_{a\text{-}b}(T)$ dependence and for the asymmetrical shape of oxygen profile observed in our LW devices, as shown in Fig. 3.

Our result is an additional direct evidence that laser light assisted rise in temperature of the YBCO film can affect increase in activation energy of atomic oxygen diffusing along the direction not only perpendicular and also parallel to the *a-b* plane [16]. The defects of the YBCO MOCVD film, like, e. g., screw dislocations and grain boundaries, can channel the diffusing oxygen along their directions [14]. The channeling of oxygen diffusion along defects leads to a asymmetric profile of the LW line resulted by a non-uniform oxygen distribution.

4. CONCLUSIONS

We report on investigation results of remnant oxygen content in optically-modified regions of the 0.3-μm-thick YBCO films by means of an LW technique in an inert gas ambient at room temperature. Optically induced heating affects nonuniform diffusion of oxygen in the film and nonuniform distribution of remnant oxygen content depending on a 532-nm-wavelength cw-laser illumination power.

A level of oxygen depletion and a size of the laser-written regions in the YBCO film can be directly estimated from spectra of SEM with X-ray microanalysis technique, while the residual oxygen content in the tested film can be estimated assuming a correlation between the remnant oxygen content and electric transport properties of the oxygen-deficient YBCO film.

Three-dimensional defects of the YBCO film grown by means of the MOCVD technique, such as screw-dislocation and grain boundaries can channel the diffusing oxygen along their directions. The channeling of oxygen diffusion, in turn, affects an asymmetric profile of the LW line and asymmetry in distribution of oxygen in the film.

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