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Manufacturing Technology of the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ High-Temperature Superconductor

Yury Evgenevich Grigorashvili

National Research University of Electronic Technology
Russia

1. Introduction

Practical use of high-temperature superconductors is considerably limited by the available technology to fabricate superconductors with characteristics, suitable for use in electrical products and electronics applications. All known high-temperature superconductors, which have critical temperature above the boiling point of nitrogen (77 K in normal conditions), consist of complex elemental composition and crystal lattice. All types of high-temperature superconductors are fragile.

Nowadays the most advanced technology in manufacturing the high-temperature superconductors and their products is done for the $Y_1Ba_2Cu_3O_7$ (Y-123) system. These are conductors of the second generation, multi-layer electronic structures, and devices with SQUIDs base. However, the temperature change of this system into the superconductive state is about 90 K. If affordable nitrogen is used to cool down the system, the working temperature difference would be just 14 percent shy of the critical one. Also, operational reliability is insufficient.

The high-temperature superconductor of the following composition - $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) is the only one having the temperature in superconductive state above 100 K. Experimental data and research allow us to consider the creation of commercially-viable technologies based on the use of this superconductor. This superconductor has 30 percent operational reliability in temperature. It is also degradation-resistant under normal weather conditions. Yet, very limited research records exist in forming this high-temperature superconductor.

This chapter contains research results that focus on commercial implementation of technology that is based on manufacturing structures with the Bi-2223 superconductor, which are used in electronic industry. In this chapter we report the study results of the volume formation of the 110 K superconducting phase, including influences of lead, silver, and fluorine.

We show the process of obtaining thick films on inert substrate. Major attention is given to a manufacturing technology of epitaxial, thin, single-phased and defect-free layers situated on a monocrystal lattice. Also, additional information is included on its electrical and magnetic properties, as well as the analysis of possible implementation into electronic technology.

2. The manufacturing technology of superconductive structures with (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ composition

In order to make high-quality superconductive structures on a monocrystal substrate we need to collect the information on processes happening during the crystal structure formation, the influences of material composition and dopants, manufacturing methods and technological conditions, as well as obtaining of electro-physical and magnetic properties in samples. In this chapter we describe the manufacturing technology of Bi – 2223 high-temperature superconductor and its structures that can be used in electronic industry (Grigorashvili, Y.E., Volkov, S.I., 1999; Grigorashvili, Y.E., 2005; Grigorashvily, Yu.E., Ichkitidze, L.P. & Volik, N.N., 2006).

2.1 The formation of superconductive phases in bulk material

Bulk material synthesis allows us gather information easily on the formation of high-temperature superconductors of various compositions and on optimal technological modes of thermal treatment. During the manufacturing process bulk material presence neutralizes changes in material surface structure. Prepared samples have dominant bulk properties as opposed to boundary properties.

This section describes the technology of making bulk superconductors of Bi-2223 composition, using methods of solid-phase synthesis. The original research results show the impact of developed technology on the formation of different superconducting phases in the BSCCO system. The conducted research determined the effect of lead and silver doping onto electrical characteristics of samples, including critical temperatures in the beginning and end of the superconductor's transition and critical currents in magnetic fields.

The first stage in bulk superconductors manufacturing is the production of micro dispersive charge of stoichiometric composition. In our research the charge was obtained from nitrates in metals. First, the manufacturing of nitrates mixture was done in proportions stated in 2223 formula for metals. In order to get rid of water and partial nitrates' decomposition the mixture has been annealed at 400 ^{0}C for two hours.

Formed spec grinded and the mixture stirred. The average size of grains in powdered mixture measured 4.5 µm. The second thermal treatment has been completed in oxygen atmosphere in 16 hours at 810-850 ^{0}C temperature range. The manufactured charge had superconductive properties. It was registered with diamagnetic response. The method of such diagnostics is presented in (Afanasev & Chaplygin, 1992).

Pellets were pressed from the charge into shapes sized 12-20 mm in diameter and 3-5 mm in thickness. The pellets were annealed in a gas mixture of nitrogen and oxygen in 10 to 50 hours under 800-850 ^{0}C. It was experimentally proven that the superconductive phases appear after a 20-hour annealing in temperatures registered above 820^{0}C. It is proven by temperature dependence on diamagnetic response and direct current resistance. The content of superconductive phases rises in relation to time of thermal treatment. Yet, their amount is small in comparison to the volume of charge. Based on measured results of diamagnetic response, their bulk makes about 15 percent at 849 degree C thermal treatment in 50 hours.

Right after the discovery of Bismuth-based superconductor it was determined that the lead presence considerably speeded up the process of superconductive phase formation (Sunshine S., et al., 1988). In our experiments lead was injected either as an additional element or as partial substitute for Bismuth. The amount of lead and Bismuth varied between 2/0.4 and 1.4/0.7.

Just like in previous case the pellets were pressed from powder, which were annealed in argon, oxygen, and air atmospheres. It was shown that the argon atmosphere annealing produced slight melting of pellets. Yet, under the oxygen atmosphere annealing the pellets' sides remained sharp and even. However, the amount of superconductive phases was too small in both cases. The best results were obtained during the annealing of argon and oxygen mixture with a partial pressure of 0.8 and 0.2 respectively. Similar results were received after annealing in air atmosphere.

(a)   (b)
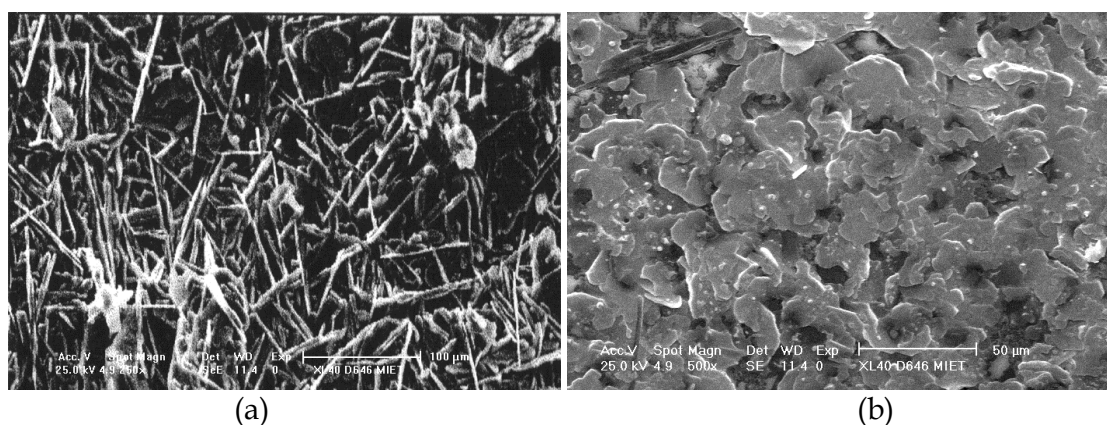
a – $Bi_2Sr_2Ca_1Cu_2O_8$ Phase. Crystals are in a shape of needle-like crystallites.
b – $Bi_2Sr_2Ca_2Cu_3O_{10}$ Phase. Crystals are in a shape of platelet crystallites.

Fig. 1. The superconductor's surface morphology of Bismuth system.

It's important to notice that the formation of Bi- 2212 phase happens when the temperature range of annealing is between 820 - 840 ^{0}C. The surface morphology of such samples has needle-like crystallite appearance (Fig. 1a). Needles' diameter is 2 to 4 µm and their length is 10 to 15 µm. The resistance dependence on temperature is shown in a spike that starts at 90 K temperature and ends at around 80 K (Fig. 2). The increased time of annealing does not lead to a temperature increase in the beginning of transition into a superconductive state.

The process of annealing at 840-860 ^{0}C temperature range forms a two-phase system of Bi- 2212 and Bi- 2223. It is shown with two little steps situated on curves, explaining resistance dependence on temperature (Fig. 2). There is a formation of the through channel at a superconducting temperature reaching near 110 K during the 30-hour annealing at 860 ^{0}C. Critical current density is above 10^4 A/cm². It's typical for these samples to have crystallite formation in a shape of flat disks (platelet crystallites) that are 15-20 µm in diameter and 1-2µm thickness (Fig. 1b).

The results of experimental research show that it's difficult to make the Bi-2223 mono-phased material. Diamagnetic response measurements prove existence of two phases with critical temperatures measured at 110 K and 85 K. The synthesis of superconductive phase is very long and demands thermal treatment maintenance locked in a very narrow range.

With a temperature range at +/-0.5 at 860 ^{0}C and the process of annealing around 100 hours the samples can be made with the superconducting state transition beginning at 115 K and completing at 108 K respectively. General findings in literature mention the development of bismuth-system phase with a critical temperature transition at only 110 K.
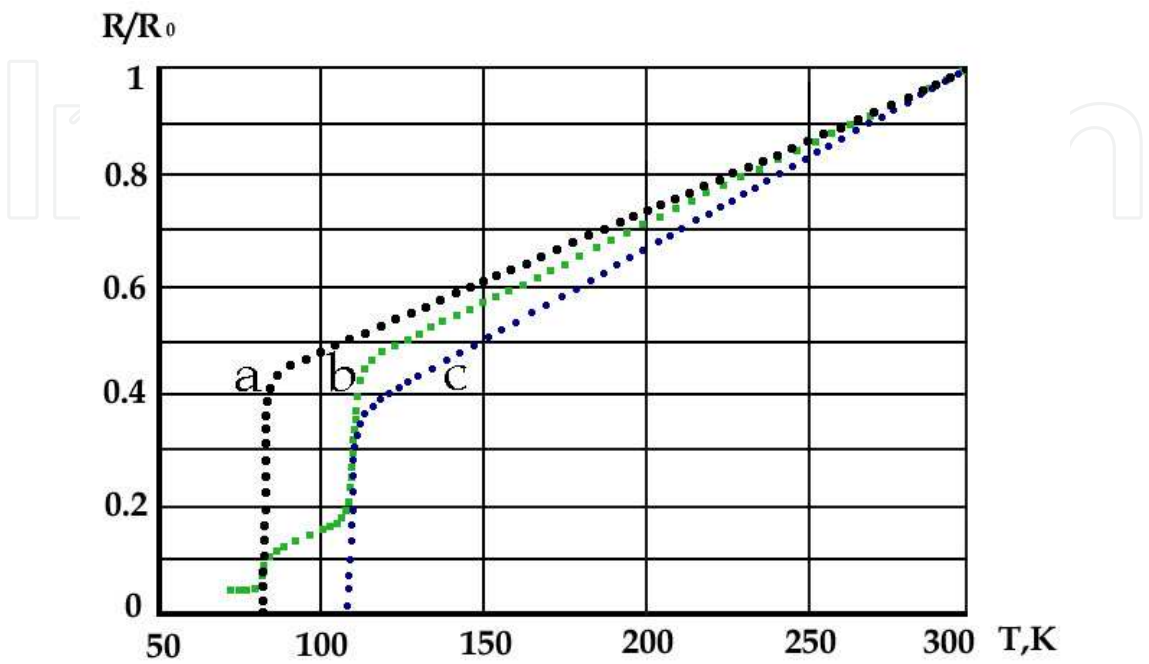
a – $Bi_2Sr_2Ca_1Cu_2O_8$ phase; b– mixture of two phases c - $Bi_2Sr_2Ca_2Cu_3O_{10}$ phase.

Fig. 2. Ceramic pellets resistivity dependence on temperature at various modes of annealing.

The author researched the opportunity of getting new characteristics of Bismuth system where the oxygen was replaced by fluorine. The samples were manufactured using the same technology mentioned above. Considerable superconductor volumes were not present. Alloying of silver powder with an atomic fraction of up to 0.5 increased the critical current density over 10 times.

2.2 Formation of bulk superconductors on a solid substrate

Next step in technological development of Bi-2223 formation is the creation of a bulk superconductor on a solid substrate. In this case, the processes described above should remain the same but the new sample would have a double-layer structure. To meet the described conditions, it's necessary to make an inert substrate relative to metals and their oxidations, entering the superconductor.

Bulk-layered Bi-2223 superconductor with a solid substrate was manufactured using a two-step system. First, the mixture was placed on a substrate, and then, a high-temperature annealing was carried out. This approach allowed us to divide the problem into two parts and research the conditions of each part separately.

The thickness of a deposited layer was several hundred microns. Such layer may be considered as a bulk one with the condition that there is neither interaction nor interfusion of the mixture at the superconductor-substrate border.

Widely accepted substrates of monocrystal silicon, oxidized silicon, and sapphire get mixed with superconductor's metals and its oxidizers at temperatures above 500 ^{0}C. Chemically inert substrates are MgO and SrTiO$_3$ monocrystal substrates.

Aerosol method is used to spray the oxides of metals onto the substrate. It is achieved by sputtering the microdrops of the solution with metal salts and their oxidation onto a hot substrate. The composition of the solution was chosen in such a way that when the microdrops hit the hot substrate, evaporation of a solvent, decomposition of metals' salts and the formation of oxide mixture took place.

The diagram of a unit, illustrating the manufacturing of films using aerosol method is shown at Fig. 3. The source is 0.05M water solution of lead nitrate, strontium, calcium, bismuth, and copper with added nitric acid and acetic acid. Ultrasonic disperser was used to make the aerosol. The aerosol mixture was delivered to the hot substrate via inert gas. In experimental research the substrate was heat-treated at 820-830 ^{0}C temperature. It required use of a silicon carbide heater that was able to work for a long time in aggressive atmosphere. The evaporation of water occurred at high temperature when water-drops reached the substrate. After that the nitrates decomposed and oxides developed. To increase the size of area of homogeneous deposition and maintain high temperature of a substrate, the aerosol nozzle scans the surface in two coordinates.

In experimental research the power of ultrasonic transmitter, speed of gas current, temperature of a substrate, frequency and range of scanning, and composition of a solution were varied. The composition of obtained films was controlled by chemical methods and the X-ray specter microanalysis method.
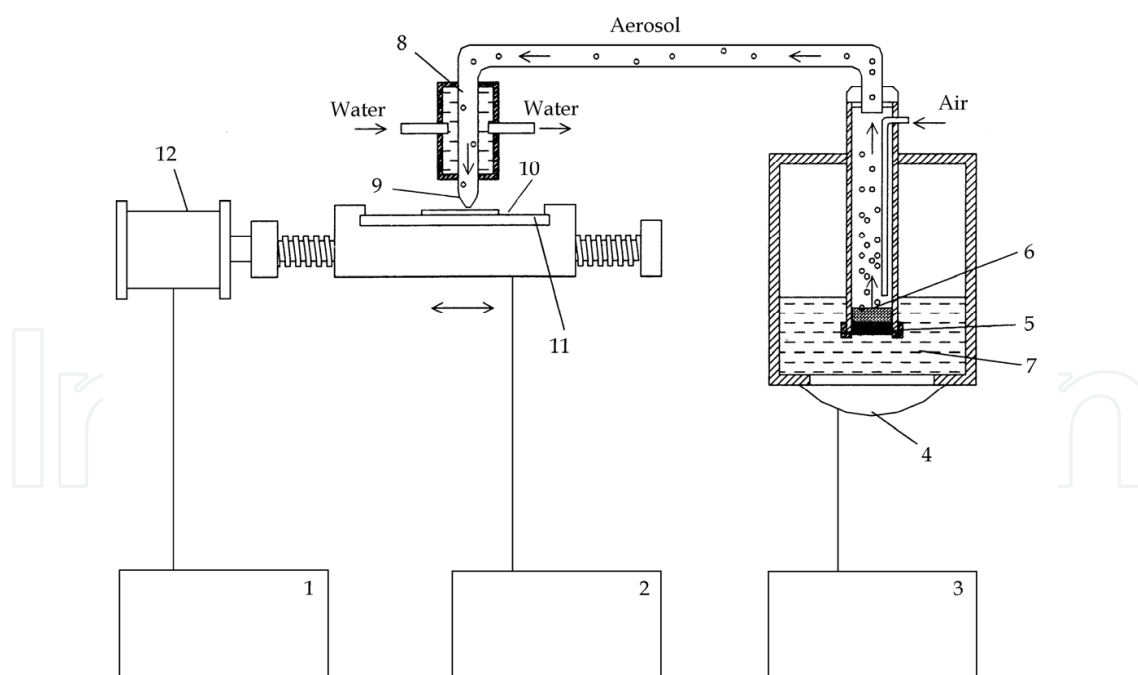
1- Control unit of the mechanical scanning system. 2- The temperature controlling unit. 3- High-frequency generator 12.6 MHz, 4- piezoceramic transmitter, 5- membrane, 6- the salt solution of basic metals. 7- water. 8- water refrigerator. 9- nozzle. 10- substrate. 11- Lamellar heater. 12- step motor.

Fig. 3. The diagram of a device showing the deposition of a bulk-layered superconductor on a substrate.

Main advantage of the described method is the simplicity of making changes in film composition. It is achieved by a varied concentration of basic metals' nitrate salts in a solution. The second important advantage of this method is the ability to make compositionally homogeneous layers in a big area.

Manufactured layers had amorphous structure of oxide mixture of basic metals. To form the crystal structure of Bi-2223 superconductive phase we used annealing in a mixture of either oxygen and argon, or 0.2/0.4 nitrogen. During the process of annealing there is a partial loss of bismuth, lead, and copper. That is why the aerosol mixture had enrichment with salts of listed metals at the depositional stage.

Film resistivity dependence on temperature with annealing modes that result in Bi-2223 phase formation is shown on Fig. 4. As seen on this picture the formation of superconductive phase is noticed after 10 hours of annealing. It is accompanied by appearance of graph zones with sharp decline of resistance at 110 K. There is a proportional increase of a superconductive phase during further annealing. Fair superconductive through channel forms after 50 hours of annealing.

Major disadvantage of this method is the difficulty of forming films with even relief. Superconductive 1-2 μm-thick layer had a bumpy surface of about the same height. The reduction in thickness by up to 0.5 μm decreased the height of unevenness. However, some zones appeared free of any superconductive phase on a substrate's surface.
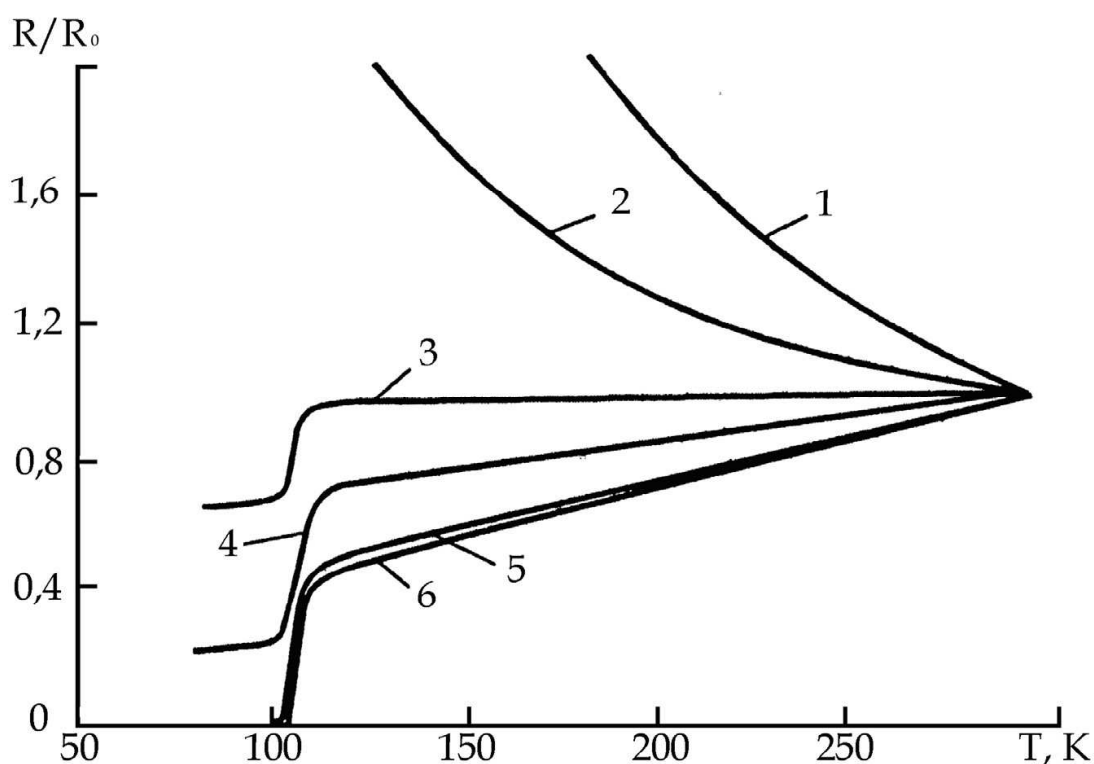
Period of annealing is 3, 5, 10, 20, 50, 100 hours. Curves are 1….6 respectively.

Fig. 4. Sample resistivity dependence on temperature at various annealing periods. Annealing temperature is 860 ^{0}C. R_0 – is the resistance at room temperature.

2.3 The technology of manufacturing thin film superconductors Bi-2223

During our preliminary research for this chapter we studied the available publications on manufacturing technology of Bi-2223 thin films. Publications were studied for 1990-2011 period in the following journals: Supercond. Sci. Technol., J. Appl. Phys., Appl. Phys. Lett., IEEE Transactions on Magnetics, IEEE Transactions on Applied Superconductivity, Physica C: Superconductivity and its Applications, Journal of Alloys and Compounds, Journal of Crystal Growth, Thin Solid Films, Journal of Vacuum Science & Technology A, Semiconductors, Technical Physics. Besides journal publications, we also studied the U.S., European and Russian patents.

It's worth mentioning that almost all publications on thin film manufacturing are for the Bi-2212 system. There are just a few publications available that have printed the results on thin film manufacturing with thickness less than 100 nm and critical temperature above 100 K. The problem of the formation of a superconductor Bi-2223 with a superconducting transition temperature above 100 K on single-crystal substrate remains topical today.

2.3.1 Basic methods of thin film manufacturing

Method of molecular-beam epitaxy (MBE) was developed in the beginning of the 70-s for manufacturing of high-quality, very thin films (Cho, A. Y., Arthur, J. R., 1975). This technology was used by a number of authors for BiSrCaCuO superconductive film manufacturing (Steinbeck, J., 1989; Yoon, D.H., Agung, I., Saito, M., Yoshizawa, M., 1997; Zakharov, N.D., Hoffschulz, H. et al., 1997). In this technology, the evaporation of individual components of the superconductor material is made from separate the Effusion (Knudsen cells). The composition and structure get formed by continuous opening of these cells for a required amount of time. (Varilci, A., Altunbas, M. et al., 2002) Working in MBE method BiPbSrCaCuO films were manufactured on MgO substrates (001). There were received critical temperatures of 105 K and current of 6×10^4 A/cm^2. However, MBE method uses very expensive and complex equipment. Thus it's practically important to develop the alternative technologies of manufacturing superconductive thin film structures.

The technology of laser deposition (PLD) of BiSrCaCuO system films was used in this research (Ivanov, Z. et al., 1989). The process of film deposition consists of target material evaporation with a laser-radiation at energy density above 1 J/cm^2. There are excimer lasers - ArF ($\lambda = 193$ nm), KrF ($\lambda = 248$ nm), and XeCl ($\lambda = 308$nm) used for film deposition as well as infrared CO_2 lasers ($\lambda = 193$ nm). HTSC-film growth occurs at molecular oxygen pressures around 10 Pa.

This method has a number of important advantages. Thanks to having a laser radiation source outside the working chamber, the deposition process occurs in "clean" conditions. Laser beam with optical system is focused onto a small area using small-diameter targets that increase the process of efficiency in superconducting film manufacturing. Laser evaporation lets us manufacture multi-layer structures easily that consist of multi-component material (Jannah, A.N., 2009). Pulse-controlled laser radiation lets us determine precisely the thickness of the growing film.

In a study (Pilosyan, S.H., 1990) the manufacturing of $(BiPb)_2Sr_2Ca_2Cu_3O_{10}$ films is on MgO substrates (100) with Tco=110 K and Tce= 105 K parameters. Working pressure in a chamber during the deposition is 10^{-1} Torr. The impulse energy is 0.05-0.11 J at the frequency of 15 Hz

pulse repetition rate. Target-substrate distance is 20-25mm. Thermal treatment of films occurs at 850 ^{0}C temperature. It is 3 hours long. It's necessary to point out that in this process the target of Bi $_2$Pb$_{0.5}$Sr$_{1.4}$Ca$_2$Cu$_{3.6}$O$_x$ composition was used.

Main disadvantage of the PLD method is the existence of clusters (drops) found in evaporated material. It happens because of high density of laser- radiation energy. Attempts to reduce the amount of microdrops via the reduction of energetic density current, lead to an increase in a non-stoichiometric component in a depositional condensate on a substrate. It limits dimensions of substrates that can be used for high-quality film manufacturing. Usually they don't exceed 10 mm in diameter.

Among chemical methods used for Bi-2223 film manufacturing we can highlight Liquid epitaxy (Pandey, et al., 1994), Spray Pyrolysis and the deposition from gas-vapor mixture (Kimura, T., Nakao, H. et al., 1991), including the MOCVD metalorganic compounds (Stejskal, J., Leitner, J.J. et al., 2000). In the MOCVD method, the components of superconductive film are transported into a reactor in a shape of gases of metalorganic volatile compounds. They are mixed with gaseous oxidizer resulting in gases' decay either inside the reactor with hot walls or on a heated substrate and the HTSC-film formation.

The advantages of this method include: the ability to make deposition of material onto substrates of large scale, production of homogenous layers in thickness and composition, and the ease of equipment use. At the same time, data found in publications shows that manufactured films are of low-quality. They contain non-superconductive inclusions, the surface has considerable unevenness, and there is no data available on the Bi-2223 phase formation.

Method of thermal deposition of material is the most simple and inexpensive resource for BiPbSrCaCuO film manufacturing. There are several types of used sources, including resistive evaporators, flash evaporation, ion beam (electron beam) evaporators and crucibles with radioactive and high-frequency inductive heating.

In a study (Azoulay, J., 1989) the researchers made BiSrCaCuO films using resistive heating of tungsten boat, with a source crucible of Bi$_{2.3}$Sr$_{1.5}$Ca$_1$Cu$_3$ material composition. After the deposition process, films were thermally processed in an oven at 725 ^{0}C for 15 minutes and 840 ^{0}C for 5 minutes. Typical superconductive temperature reaching the superconductive state T$_{ce}$ was around 78-K for ZrO$_2$ substrates and 88-K for SrTiO$_3$ substrates.

Similar film parameters (Tce = 78K) are listed in (Patil, J.M., Bhangale, A.R. et al., 1993) that were manufactured with thermal deposition onto MgO substrate (100). In a study (Silver, R.M., Ogawa, E.T., Pan. S. de Lozanne, A.L., 1991) the BiSrCaCuO manufacturing in situ was completed using thermal evaporation method with high-frequency plasma generator. The device was constructed to make plasma at a distance from a substrate in order to stop recombination of oxygen atoms. After the deposition at 600-660 ^{0}C temperatures, films were annealed at 850 ^{0}C. The dominant phase was 2212, while the 2223 phase was present in small quantities. Similar critical temperatures were produced in studies (Basturk, N., 2005).

The analysis of conducted studies shows that high-quality HTSC-film with Bi-2223 phase and T$_c$ around 110 K remains unresolved. To find a compromise solving a problem of Bi-2223 superconductor manufacturing might be the use of magnetron sputtering method.

2.3.2 The magnetron sputtering method – The computer model for the sputtering process

Magnetron sputtering for superconductive film manufacturing is used in modes of constant current (Schultz et al., 2001) and alternating current (Grigorashvily, Y.E., Volkov, S.I., Sotnikov, I.L. & Mingazin, V.T., 1999; Grigorashvili Y.E., Bukhlin, A.V. & Veryuzhskii, I.V., 2010) with the use of one or several sources (Kuroda, K., Kojima, K. et al., 1991). In this research the following strategy of forming Bi-2223 thin films with superconductive temperature around 110 K on a 40mm-radius substrate was used:

1. Film manufacturing was complete in two stages. First stage included the deposition onto a substrate's surface of a mechanical mixture of metal atoms and their oxides of stechometric composition. The second stage consisted of the crystal lattice formation of superconductive phase.
2. Method of magnetron sputtering is used for deposition of metals onto a substrate.
3. Target composition corresponds to $Bi_2Sr_2Ca_2Cu_3O_{10}$ superconductor composition.
4. Annealing is used to form structure. During this process the stimulation of epitaxial expansion of superconductor's thin layer takes place on a substrate.

The construction and technology of magnetron sputtering unit should take into account features of a problem, such as the formation of a five-component mixture of oxide metals on a substrate with various physical and chemical characteristics. To justify the construction of the sputtering system via experimental research is extremely expensive. Thus this research process consisted of experiments with the use of a mathematical model of transporting metal atoms from a target onto a substrate.

The most advanced mathematical model of the process of solution transportation with magnetron sputtering belongs to Volpyas (Volpyas, V.A. & Kozirev, A.B., 1997). It was supplemented in accordance with this research problem-solving.

The computer model of the sputtering process used in this research had the following algorithm:

- Calculation of magnetostatic field vector in magnetron source with a complex configuration of a magnetic conductor.
- The calculation of evaporation speed from the target's surface of various atoms' types depending on the coordinates with axisymmetric system.
- The calculation of atoms' movement from the target to the substrate. In this section the computer model was used to imitate the movement of each atom from the moment of leaving the target, trajectory change during the collision with gas atoms, conditions of return to the target or adhesion to a substrate, transition to evacuation system. Atom's type for each of five components was considered as well as speed distribution and the angle of departure from a target. To determine the angle of scattering we used the quasi-hard sphere potential (Volpyas, 2000).

The model allows to determine the thickness of sputtered layer precisely and the stoichiometry of composition depending on coordinates on a substrate. Partial pressures of argon and oxygen can vary in range widely, depending on the conditions of collision-free sputtered atoms until their complete thermalisation.

Computer model was used to calculate the construction of magnetron source, substrate's position, and the pressure range of gas mixture. The magnetron source type, magnetic fields' configuration, and calculated profiles of sputtered film in a multi-component system are shown at Fig. 5.
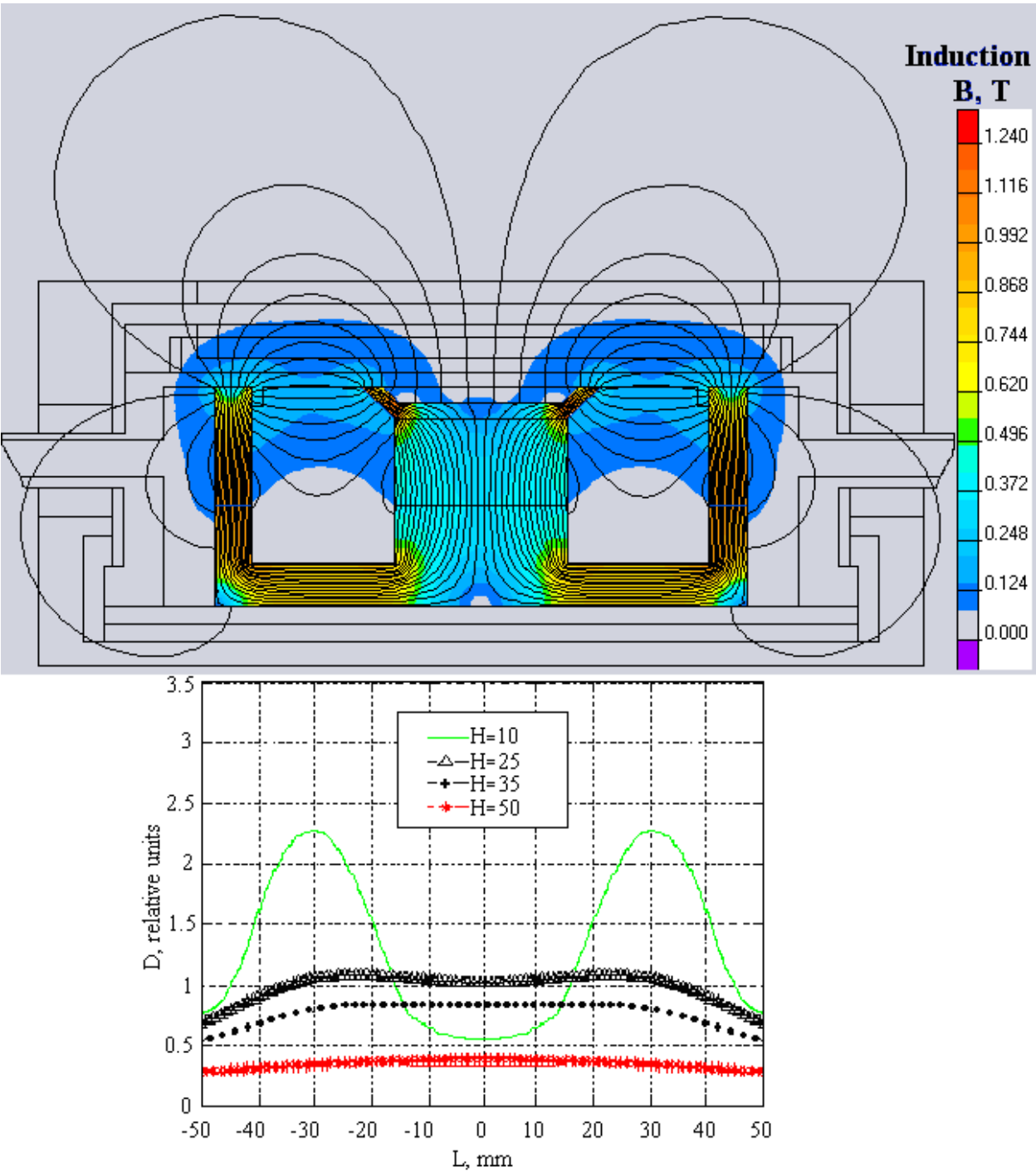

Fig. 5. The construction of magnetron sputtering system. The magnetic field induction is shown in magnetic conductor and inter-electrode space. The graphs illustrate the thickness of sputtered layer dependence on the target-substrate distance.

2.3.3 The influence of technological regimes onto composition of the multi-component mixture

In order to shorten time and reduce material expenses while searching for optimal gas pressures, we used method of planned experiment (Adler, Yu.P., Markova, E.V. & Granovskiy, Yu.V., 1976). The following arguments were chosen: the relationship of partial pressures of argon and oxygen - $P(O_2/Ar)$ and the overall pressure of gas mixture $(Psum)$. The response function consisted of atomic concentration of each component of sputtered layer.

Method of planned experiment assumes to find the analytical dependence between function of response and varied arguments (Mongomery, D.C., 1980). The input information for obtaining such correlations comes from experimental results, received in limited quantities of points of argument values. In our research we needed to find concentration correlations of each component (5 in total) in relationship to partial pressures of oxygen/argon and the summarized pressure of gas mixture. Next, we used the optimal plan D that works well is conditions under considerable influence of the noise factor (Mongomery, D.C., 1980).

During the development of matrix of planed experiment it was important to consider that the expected effect of one factor depends on the level at which the other factor is located. Thus we have the effect of reciprocity of two factors. To quantitatively determine the effects of reciprocity is to use a full-factor experiment. The planning matrix is shown in a table 1. It consists of four real experiments.

Experiment's number	X_0	Psum	$P(O_2/Ar)$	Psum *$P(O_2/Ar)$	C_i
1	+1	+1	+1	+1	C_i (1)
2	+1	-1	+1	-1	C_i (2)
3	+1	-1	-1	+1	C_i (3)
4	+1	+1	-1	-1	C_i (4)

Table 1. The matrix of planned experiment

Here C_i (N) is the atomic concentration of i-component in experiment number N. When i equals 1,2,3,4 (i = 1,2,3,4) the concentration corresponds to (Bi,Pb), Sr, Ca, Cu elements. Arguments' values are both on the upper level (+1) and lower level (-1). Quantitative values of these levels are determined by expert estimation. The regression equation for this experiment looks like this:

$$C_i = b_0X_0 + b_1P_{sum} + b_2P(O_2/Ar) + b_{12}P_{sum} \cdot P(O_2/Ar) \tag{1}$$

Coefficients of variables b_0, b_1, b_2, b_{12} are determined by standard procedures method of planned experiment.

To lay out a plan of the experiment it's necessary to determine a varied range of arguments. The criteria for range determination include the following: stability of magnetron discharge, absence of electrical gaps between the electrodes, reasonable timeframe of the process, and the formation of the depositional layer in a shape of metal oxides. Last criterion is determined by stage characteristics of a crystal structure formation. If the depositional film has oxygen deficit, then the intensive evaporation of Bismuth and lead takes place during the annealing stage. It leads to stoichiometry disturbance.

For the first approximation the following values of arguments were chosen: lower level - $P(O_2/Ar) = 0.2$; $P_{sum} = 5$ Pa and the upper level $P(O_2/Ar) = 0.8$; $P_{sum} = 8$ Pa.

Four experimental tests were performed according to a plan shown in a table 1. Before each experiment the target was sputtered onto a shutter for 50 hours to level out the surface concentration of components. In all four experiments, atomic concentrations of metals did not match the 2223 stoichiometric composition. Thus, it's necessary to search for possible manufacturing regimes (modes) to make the essential mixture. To make it happen we used the regression equation analysis. Standard programs of data analysis let us receive the following equations for atomic percentages of the components:

For Bismuth and lead:

$$C_{Bi,Pb} = 2.26 + 2.28 \cdot P_{sum} - 0.068 \cdot P(O_2/Ar) - 0.443 \cdot P_{sum} \cdot P(O_2/Ar); \qquad (2)$$

For strontium :

$$C_{Sr} = 5.32 - 2.38 \cdot P_{sum} - 0.56 \cdot P(O_2/Ar) + 0.239 \cdot P_{sum} \cdot P(O_2/Ar); \qquad (3)$$

For calcium:

$$C_{Ca} = 0.73 - 2.6 \cdot P_{sum} + 0.31 \cdot P(O_2/Ar) + 0.62 \cdot P_{sum} \cdot P(O_2/Ar); \qquad (4)$$

For copper:

$$C_{Cu} = 1.72 + 2.37 \cdot P_{sum} + 0.31 \cdot P(O_2/Ar) - 0.34 \cdot P_{sum} \cdot P(O_2/Ar); \qquad (5)$$

Regression equations can be presented in graphs that let us find visually a compromised version in a choice of pressures. Color "green" represents values of stoichiometric composition components (Fig.6).

To determine the pressure area (P_{sum} and $P(O_2/Ar)$) simultaneously with all film variables corresponding to a required mixture - $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$, the data array analysis was completed, taken from the regression equation. Area configuration where the mixture conforms to required accuracy is shown at Fig. 7.

Our study of the results has shown that in order to maintain film stoichiometry - $(BiPb)_2Sr_2Ca_2Cu_3O_{10}$, the optimal pressure variables are $P_{sum} = 4.7$ Pa, $P(O_2/Ar) = 0.35$. We must mention that this point is situated on the outside of the square, rather than its inside. The square shows conditions of the initial experiment.

To experimentally test our conclusions, the target was adjusted and the sputtering was completed at the following pressures - P_{sum} – 4.7 Pa, $P(O_2/Ar)$ – 0.35. Component

concentrations were measured with the x-ray spectral microanalysis method in ten points. Average values corresponded with this formula - Bi$_{1.71}$Pb$_{0.42}$Sr$_{2.02}$Ca$_{1.99}$Cu$_{3.05}$O$_x$.

Thus, the goal was accomplished by obtaining a thin layer of oxide mixture on a substrate, in which metals content corresponded with the formula of a high-temperature 2223 superconductor.

We should point out that during our calculation of regression equations we used a variable summing up of bismuth and lead concentrations, which equals in formula to (2). In experimentally produced films we found the right correlation between bismuth and lead concentrations. In particular, the average value of bismuth is 1.7 atomic fracture and of lead is 0.4.
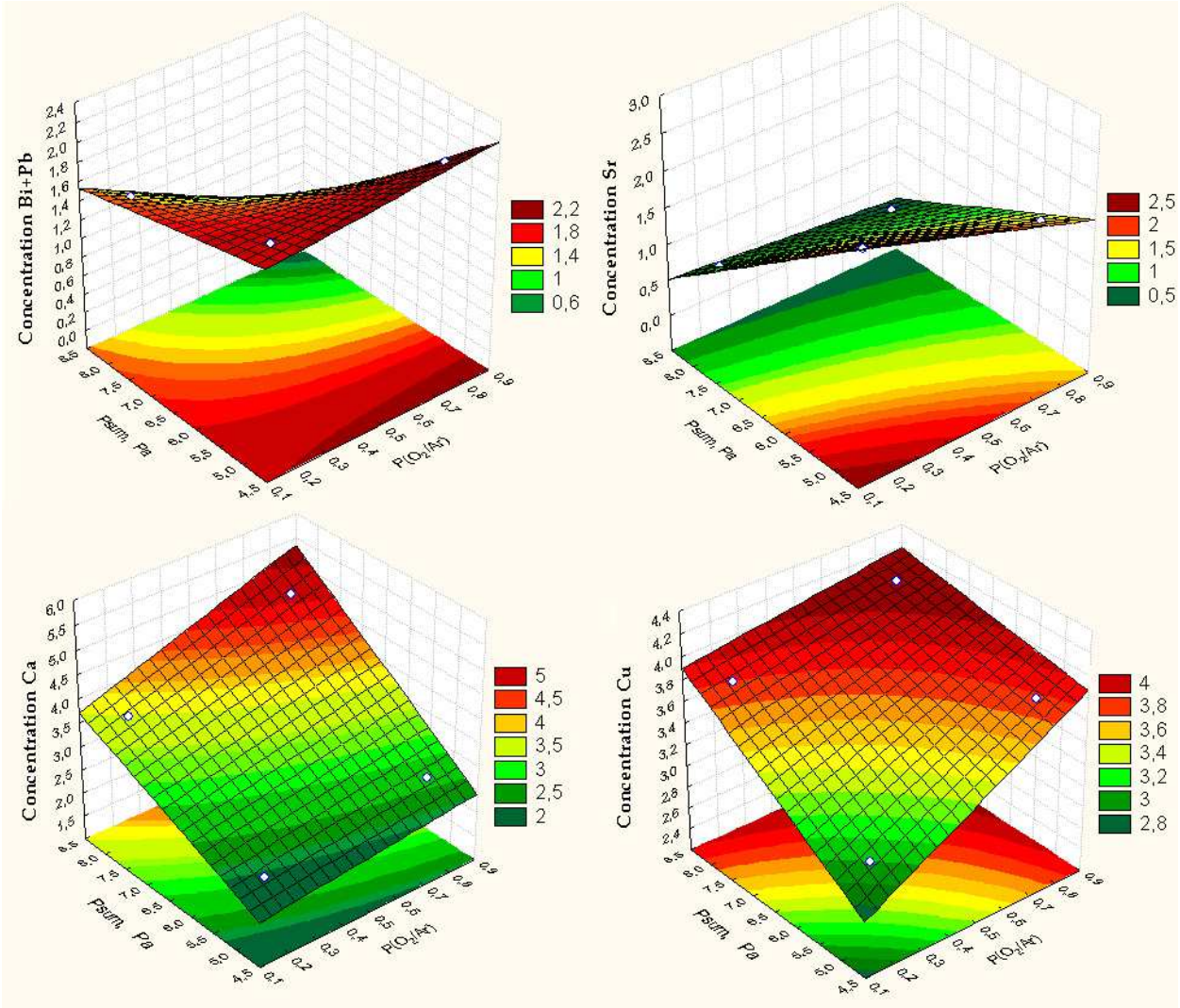
Fig. 6. Dependence of concentration of elements of a film from P$_{sum}$ and P(O$_2$/Ar).
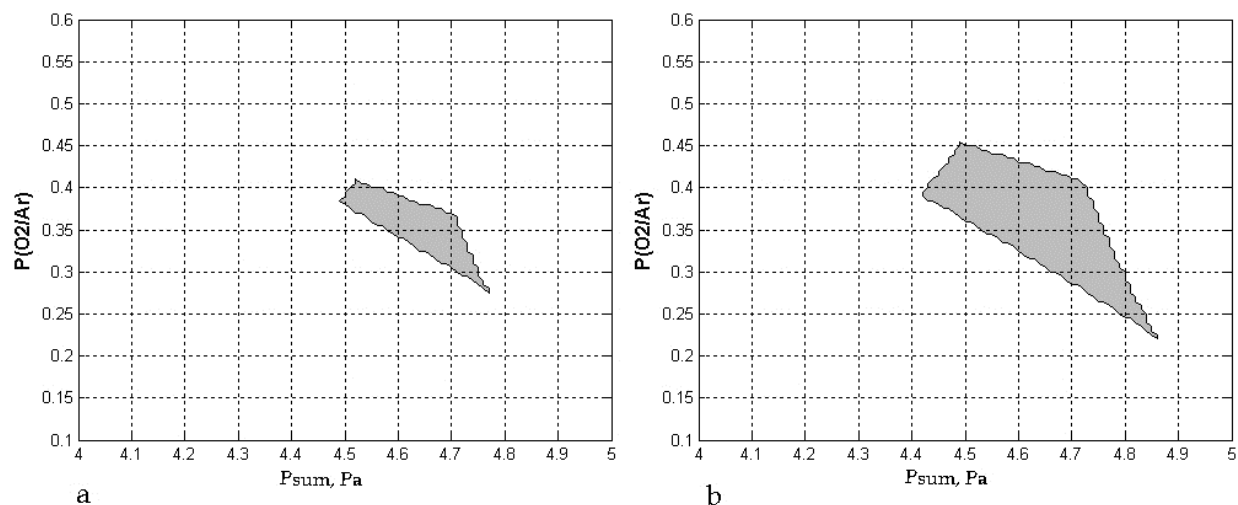
Fig. 7. The area of pressure in which deposited composition corresponds stoichiometric with accuracy: a - 4 % and b - 5 %.

2.3.4 The formation of crystal structure

It was shown in a 2.1 section that in the oxide mixtures of stoichiometric composition and temperatures above 820 C, the formation of superconductive phases takes place. The phase of Bi-2223 composition is formed at higher temperature rate of 860 ^{0}C and a narrow temperature interval. These results are taken to validate the manufacturing technology of thin film superconductive structures. Yet, there are a few considerable differences that must be taken into account.

High-temperature annealing leads to changes in composition not only at its surface, but also at its entire thickness. If the film is annealed at 850…..860 ^{0}C temperatures in an air atmosphere, then it will evaporate from a substrate's surface in a few hours of annealing. Thinly-layered silver sputtering over it doesn't impede this process.

The conducted experiments have shown that the evaporation process depends on both bismuth and lead losses. If the annealing is done in clean oxygen, then it's difficult to form 2223 phase. If the annealing is done in inert atmosphere, then bismuth, copper, and lead evaporate quickly. To stop the evaporation process by regulating the oxygen levels is not possible.

In our research to hold the mixture at substrate's surface, we used oxidized atmosphere with partial pressure of bismuth and lead equal to saturated vapors of these components at annealing temperature. If the process managed to form 2223 phase, then the structure remained stable even at high temperatures.

The Fig 8 shows the surface morphology and film resistivity dependence on temperature after various annealing stages. Low-temperature annealing leads to phase formations that become conductors in 77….300-K temperature range, Fig. 8 a. The annealing at close to optimal conditions forms 2223 phase. Yet, its grains have chaotic orientation. Moreover, there are parts with 2212 phase and other conductive phases, Fig. 8 b.
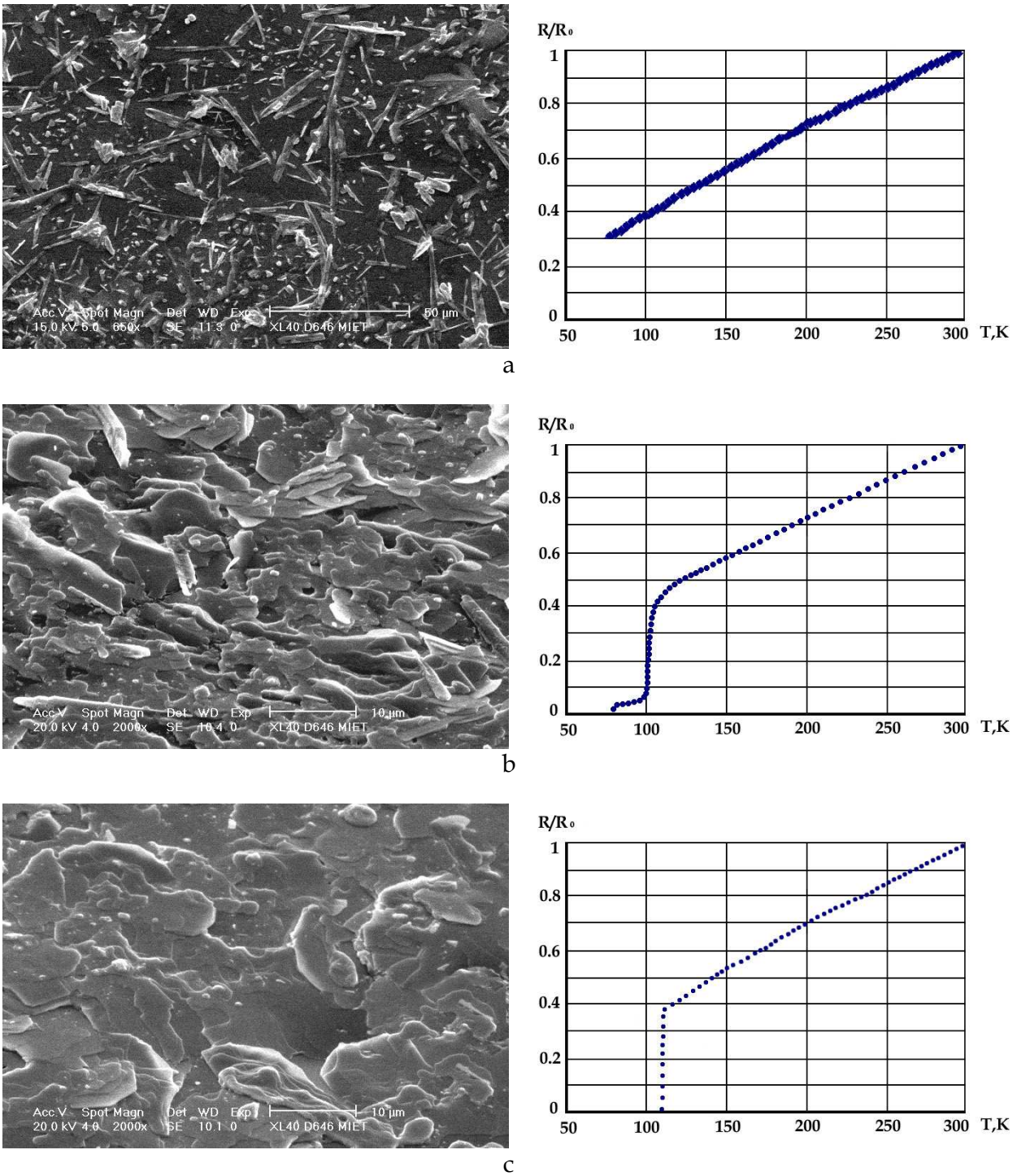
a

b

c

Fig. 8. Morphology of a surface and temperature dependence of resistance of films after various modes of annealing

Finally, the optimal annealing modes stimulate 2223 phase growth along the substrate's surface. To obtain such results we used the difference in growth speed of 2223 phase along the axis a, b and c. Grains looked disc-shaped of minor height yet big dimension, Fig. 8 c.
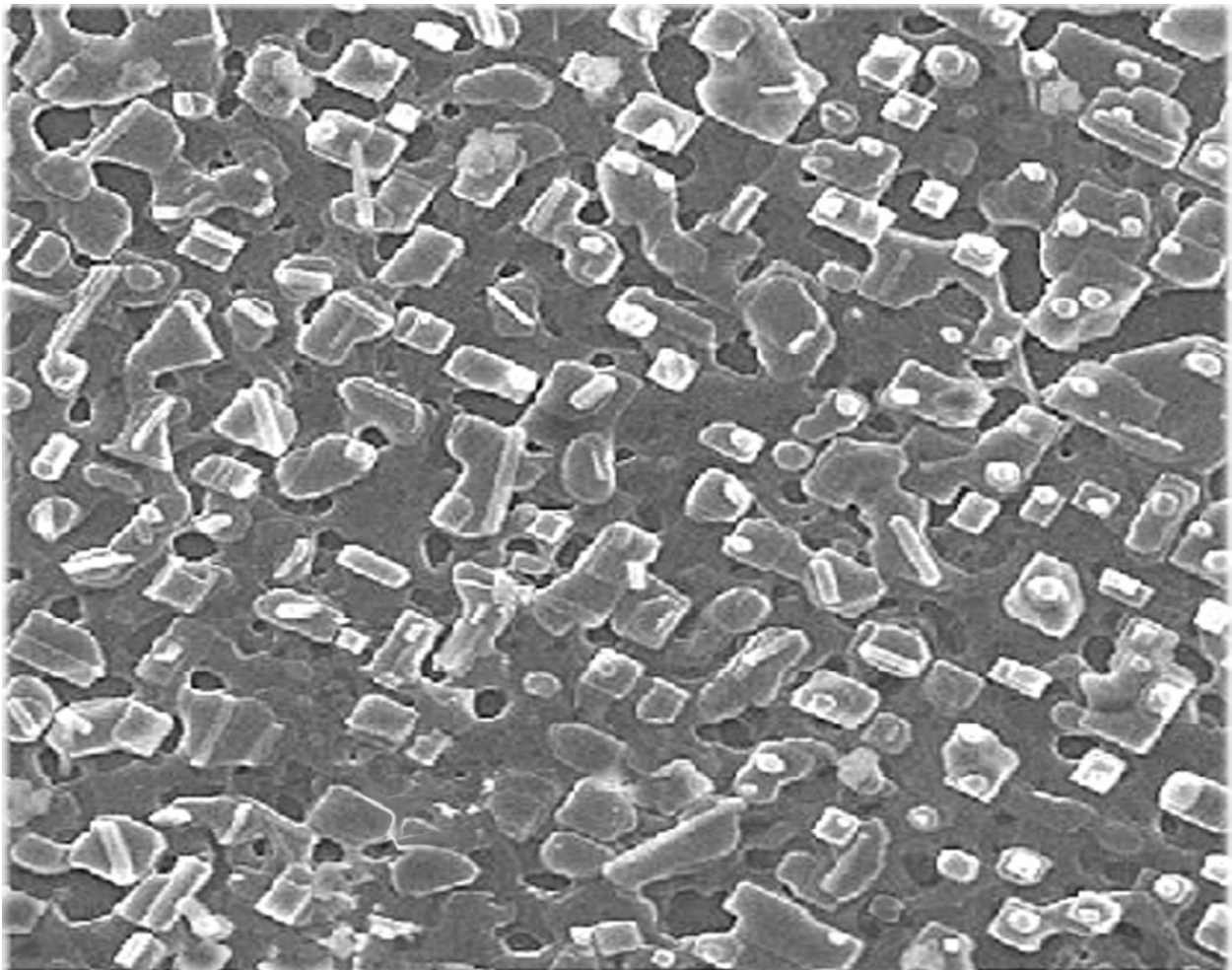
Fig. 9. Morphology of a surface of a film with the oriented grains

Using structures with sputtered films less then 100nm in thickness, the superconductive layer becomes shaped in the polycrystal units. Its orientation repeats the structure of MgO monocrystal. The surface morphology of such samples is very smooth in both electron and tunnel microscopes. During the increase in sputtered layer thickness structures arise having several storey grain formations. The example of such formation is shown on the Fig 9. The sample has continuous superconductive layer with 110 K critical temperature. Small grains located on the surface have orientation of a superconductive crystal.

2.4 Electrical and magnetic characteristics of Bi-2223 thin films

To research both electrical and magnetic characteristics of Bi-2223 films (Grigorashvily, Y.E., Volkov et. al., 2000; Grigorashvili, Y.E., Ichkitidze, L.P., Mingazin, V.T., 2004) using photolithography methods, the bridge-shaped structures were made 0.5….2.0 mm in length and 5….50 µm in width. Wide areas ($200 \times 200 \; \mu m^2$) were formed on the edges of bridges. There were two contact areas made on each field with sputtering and the following silver annealing. Measurements were taken by four probe method at a computer device. In all measurements magnetic field vector B was directed perpendicular to a transport current. Current density varied through sample in a range between $10^1 …..10^6$ A/cm^2.

All researched films had critical temperature around 110 K. Yet, technical parameter variations could considerably change the size of critical current and magnetic characteristics. The track consists of continuously connected grains of monocrystal superconductor and intergranular boundaries. These two elements behave differently. It was experimentally proven that grains remain to be superconductive at current density 10^5 A/cm^2 and constant magnetic filed 1 T. Intergranular boundaries can be either dialectical, conductive or Josephson elements. If the boundaries are resistive fields, then during the increase in current density, there is a residual current registration at temperatures below critical ones. Every boundary behaves as the Josephson junction in the intermediate condition. Overall, the entire structure can be considered as the Josephson environment. Although such boundaries reduce critical current density, they simultaneously increase the responsiveness to magnetic field. Usually magnetic response value is determined as:

$$S = [R(B)/R(0) - 1]/dB \qquad (6)$$

Here $R(0)$ – is the sample resistance in external magnetic field B_0.

$R(B)$ – is the sample resistance in magnetic field that equals to B_0+dB.

It was experimentally shown that magnetic responsiveness - S depends on sample's temperature, value of a measuring current, and the average value of magnetic field at measurements. All values had extremum in function of third variable at two other fixed variables. Fig. 10 shows magnetic responsiveness dependence on a measuring current in various ranges of measured magnetic fields.

Manufactured films have anisotropic properties in relation to the magnetic field. The Fig. 11 illustrates resistance of the microbridge change depending on the angle between magnetic field direction and substrate's surface. The resistance difference increases with the increase of magnetic field's absolute value.

Value S is managed by technological regimes in broad limits. It's possible to pick up such options when the microbridge in resistance measurement mode can be used as a magnetic field device with high sensitivity. Samples were manufactured with $\sim 4 \cdot 10^3$ T^{-1} magnetic sensitivity at 77 K temperature in magnetic fields measuring less than 100 µT. Magnetic flux sensitivity of this device is about 0.1 Φ_0.
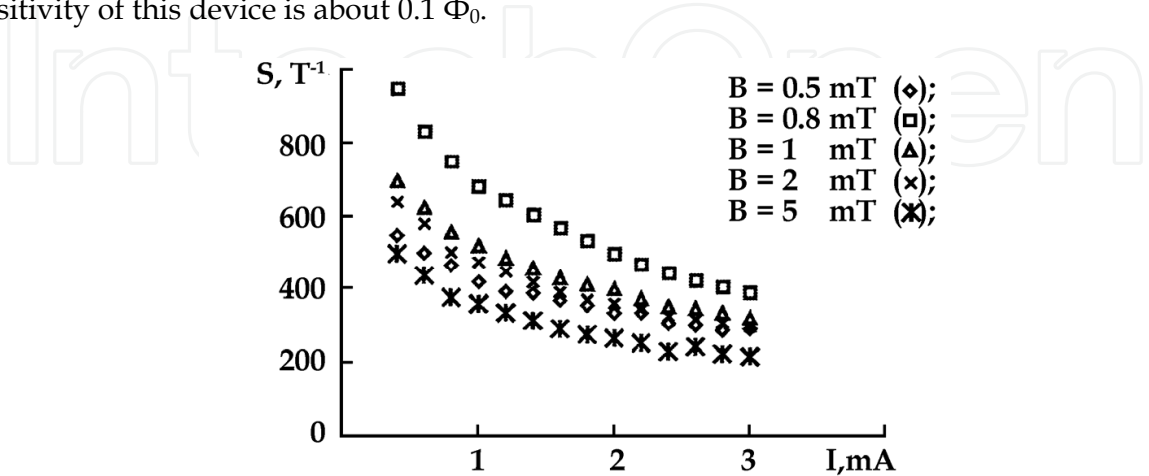

Fig. 10. The dependence of the magnetic sensitivity on the value of the measuring current in static magnetic field. The temperature is 77K.
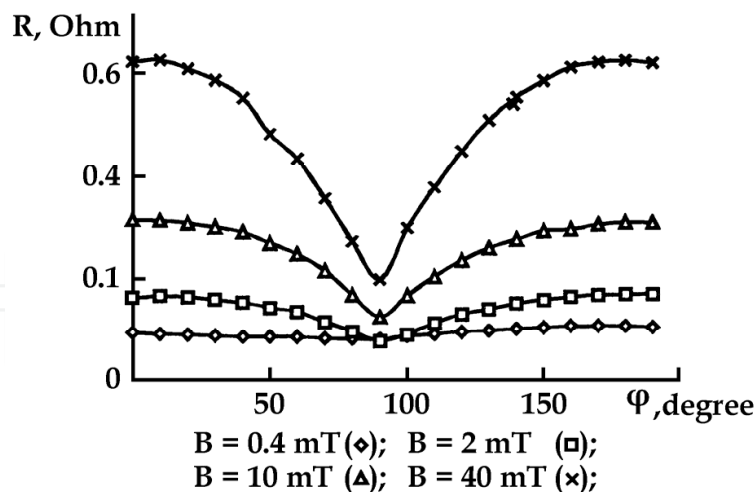
Fig. 11. Structure resistance dependence on the angle between substrate's surface and magnetic field direction. Magnetic field is perpendicular to transport current. The microbridge temperature is 77-K.

3. Conclusion

High-temperature superconductor of $(Bi,PB)_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) composition can become a useful material for creation of commercial technologies. This chapter contains research results aiming at creation of methods to form superconductor thin films for electronic structures. Thin films were fabricated on the MgO monocrystal substrate that had the most considerable content of 2223 phase. The result is achieved by precise lead doping, stoichiometry maintenance at all stages of formation, as well as creation of special conditions when growing superconductor film epitaxialy repeats the MgO monocrystal substrate and has the structure of strongly textural polycrystal. Changing technological modes, it is possible to control effectively parameters of boundaries between grains, saving thus critical temperature 110K and changing a critical current with magnetic sensitivity that is used for creation of sensors of physical values.

4. Acknowledgments

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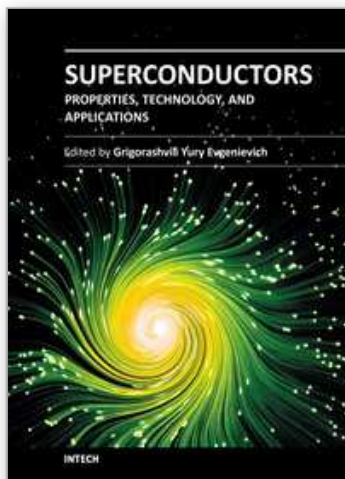
Superconductors - Properties, Technology, and Applications

Edited by Dr. Yury Grigorashvili

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