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Resistive memory physical mechanism in a thin-film $Ag/YBa_2Cu_3O_{7-x}/Ag$ structure

***Abstract**. This paper presents results of experimental research on the electro-resistance memory effect in a thin-film $Ag/YBa_2Cu_3O_{7-x}/Ag$ structure at temperatures of 78K to 300K. This phenomenon was explained by processes of destruction and recovery the oxygen-depleted layers situated close to electrodes and within the superconductor volume. The processes occur through ion electro-diffusion by numerous oxygen vacancies existing in perovskite-type materials.*

Streszczenie.** W pracy przedstawiono wyniki badań doświadczalnych zjawiska pamięci elektrorezystancyjnej w strukturze cienkowarstwowej $Ag/YBa_2Cu_3O_{7-x}/Ag$ w temperaturach od 78K do 300K. Zjawisko to wyjaśniono procesami likwidacji i odtwarzania warstw zubożonych w jony tlenu, znajdujących się w sąsiedztwie elektrod oraz w objętości nadprzewodnika. Procesy te zachodzą na drodze elektrodyfuzji jonów poprzez liczne wakansy tlenowe obecne w materiałach typu perowskitu. **(Mechanizm fizyczny pamięci rezystancyjnej w cienkowarstwowej strukturze $Ag/YBa_2Cu_3O_{7-x}/Ag$).

Keywords: high-temperature superconductors, electro-resistance memory effect, current and temperature characteristics, oxygen-ion electro-diffusion.
Słowa kluczowe: nadprzewodniki wysokotemperaturowe, zjawisko pamięci elektrorezystancyjnej, charakterystyki prądowe i temperaturowe, elektrodyfuzja jonów tlenu.

Introduction

A long-lasting competition in the field of electronics in trying to achieve greater computer memory capacities comes across significant development difficulties. The ability of minimizing the sizes and the energy needed to record and read information in traditional RAM memories based on semi-conductors, and, consequently, the possibility of enlarging their capacity have already reached their apex. Thus, increased scientific activity in search of new materials and mechanisms that could be used to build elements of RAM memory can be observed recently. The analysis of development trends in this field, carried out in [1], has led to distinguishing 10 new technologies that could soon replace the traditional ones. The use of electro-resistance memory effect seems to be one of those more promising technologies.

This phenomenon occurs in numerous materials and different temperatures (from 4 to 400 K). Oxide materials of simple crystalline structure, such as TiO_2 [2], NiO, Al_2O_3 [3,4], or materials of more complex perovskite structure, such as $YBa_2Cu_3O_{7-x}$ [5,6], $Bi_2Sr_2CaCu_2O_{8+\delta}$ [7,8], $Pr_{1-x}Ca_xMnO_3$ [9], $SrTiO_3$ [10] can be given as examples. However, the nature of electro-resistance memory effect in both groups of materials is different. In the first one, it is unipolar, and in the second one – bipolar. Moreover, materials of perovskite structure have the qualities of high-temperature superconductors (HTS). Superconducting materials have interested scientists for a long time because of their small energy loss and great speed of reaction.

The aim of this work is to present the results of experimental research of the electro-resistance memory effect in a thin-film structure based on a $YBa_2Cu_3O_{7-x}$ high-temperature superconductor exposed to current, and to explain the physical mechanism of this phenomenon.

The experiment

During the research, a sample in the form of an HTS structure consisting of a thin film of $YBa_2Cu_3O_{7-x}$ superconductor deposited on the sapphire substrate (Al_2O_3) of the size of 10x6 mm [11] was examined. The film of the superconductor of $h\approx0.5\mu m$ was obtained by the magnetron sputtering method. Crystallographic research has proved predominant orientation of the crystallite c-axis being perpendicular to the surface of the film. Then, the HTS film was formed with the photolithography method in the shape of a microbridge of the width of w=200μm and length l=2 mm, and then a layer of silver contacts was sputtered and formed (the $Ag/YBa_2Cu_3O_{7-x}/Ag$ structure). Parameters of the HTS microbridge, immediately after it was constructed, equalled: critical temperature T_c=87.5 K, superconducting transition temperature width ΔT_c=1.4 K and critical current $I_c\approx$550 mA at the temperature of 78 K [11]. The examined sample was placed in a liquid nitrogen continuous-flow cryostat, intended for measurements within the temperature range from 77 to 300 K, and attached to a “cold finger” with silver paste. During the tests, the sample remained in vacuum of 10^{-2} hPa.

Current-voltage characteristics *(I-U)* of an HTS microbridge at various temperatures and of different background of preceding influences were determined during the experiment. Measurements of *I-U* characteristics were carried out with the use of the 4-wire method, supplying the microbridge from a source working in the current stabilization mode, which is more convenient while examining the electro-resistance effect in comparison with the voltage stabilization mode. This results from the assumption (frequently proved in literature, e.g. [5,8]) that resistance changes may occur in different areas of the HTS structure and may be caused by various physical mechanisms, and total bridge resistance may be treated as a series connection of those areas. In such model, if the current is stabilized, resistance changes of one area do not cause the electric field change in neighbouring areas, which enables better identification of physical mechanisms dependent on its value.

On the grounds of current-voltage characteristics, which were obtained during the tests, resistance characteristics were determined. Maximum value of current flowing through the sample was 50mA, i.e. much lower than the level of critical current *(I_c)*. Except for *I-U* characteristics measurements, temperature characteristics of resistance within the range from the liquid nitrogen temperature ($T_{LN}\approx$78K) to the room temperature ($T_a\approx$300K) were also determined.

Measurement results

Current-voltage characteristics were determined by changing current in a cycle: from 10μA, taken as zero current, to the maximum value I_m, and then changing to 10μA again. The cycles differed with the current flow direction. The positive direction was taken conventionally, as the examined HTS microbridge is symmetrical. Under the influence of current cycles (both positive and negative) of different I_m values, *I-U* characteristics were nonlinear. The microbridge resistance in the room temperature changed from 632Ω to 291Ω and it equalled 454Ω after a few cycles. The results of further measurements are presented in Fig. 1 in the form of resistance characteristics. The order of carrying out the measurements corresponds with the order of curves and the direction of their arrows.

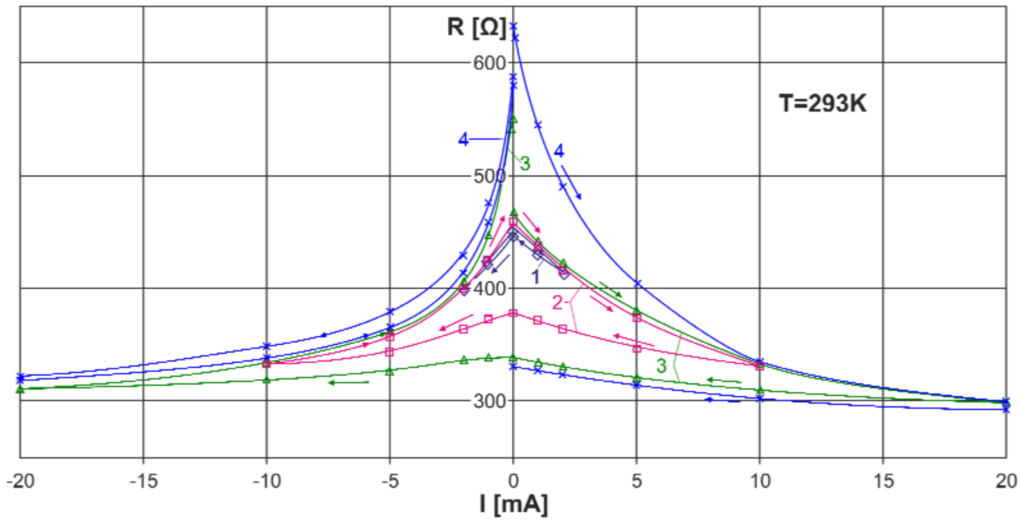

Fig.1 Resistance characteristics of an HTS microbridge in the room temperature under influence of a sequence of current cycles. The sequence of measurements corresponds with the numbers of curves and the direction of their arrows.

The phenomenon of hysteresis occurs in resistance-current *(R-I)* characteristics obtained during the experiments. The resistance values before and after a current cycle are significantly different and they change from 334Ω to 632Ω. It can be observed that the influence of a positive current cycle causes resistance switching from the higher level *(*R_H*)* to the lower level *(*R_L*)*, while a negative current cycle switches resistance into the opposite direction. Thus, the phenomenon of resistance switching in the tested HTS structure is of bipolar nature. The complete current cycle consists of positive and negative cycles (or inversely) that occur sequentially. Relative resistance changes during a complete current cycle ($\delta R_{HL}=(R_H-R_L)/R_H$) vary for the results of successive experiments (1, 2, 3, 4 in Fig.1) and equal respectively: 3, 18, 38 and 47% at I_m=2, 10, 20 and 20mA. The changes of δR_{HL} are then dependent not only on I_m, but also on the actions preceding a given cycle.

During the next current cycles of I_m not greater than 20mA in room temperature, the resistance characteristics were identical with those presented in Fig. 1, and finally, after the positive current cycle, the resistance had the value of 330Ω. During further part of the experiment, the HTS structure was cooled to the liquid nitrogen temperature, which was accompanied with the resistance drop to 172Ω. Next positive current cycle of I_m=20mA caused a slight resistance increase (up to 200Ω) (curve 5 in Fig. 2). After the direction change of the current flow, the *R-I* characteristics to -20mA was symmetrical with the previous one. However, at this point, a step change of *R* of about 100Ω occurred, up to the state of high resistance *(*R_H*)*. Decreasing the current to the zero value caused further increase of the R_H value – to 2430Ω (5 in the insert of Fig. 2). During the next cycle of negative current, the resistance characteristics ran precisely along the R_H characteristics of the previous cycle (curve 6). The following positive current cycles of I_m=20mA caused the resistance to switch to the R_L level of the 439Ω value (curves 6, 7 and 8 in Fig. 2). Gradual decrease of R_L during three current cycles can result from the dependence between the level and the time of the 20mA current activity [7]. Further influence of positive cycle of I_m, increased up to 50mA, lowered the R_L to 374Ω (curve 9). It results from the characteristics presented in Fig. 2 that at temperature close to T_{LN}, the phenomenon of resistance switching between R_L and R_H also occurs, similarly to the situation observed at the room temperature. Relative resistance changes δR_{HL}, though, reach 92% in this case (curve 6).

In further tests, *I-U* characteristics under activity of positive and negative current cycles of I_m=20mA were determined alternately with the temperature dependences of the HTS microbridge resistance within the range of temperature from T_{LN} to T_a. The results of the latter are presented in Fig. 3. The value of the measuring current was 10μA. The numbers of curves in Fig. 3 correspond with the order of carried out measurements. Because of significant steps of resistance of the $YBa_2Cu_3O_{7-x}$ microbridge at temperatures close to T_{LN}, the temperature characteristics of resistance have visibly the nature of a superconductor. The step occurs when the microbridge switches from the superconducting state (S) to normal state (N) at a given critical temperature T_c (superconducting transition). When the temperature is increased to the room temperature T_a, we can observe practically linear increase of resistance, which proves metallic character of conductivity in the N state. At temperatures lower than T_c, however, resistance does not drop to zero, which occurs in superconductors, but it takes constant, though significant, values. Dependences 10, 11 and 13 were determined after previous tests with different current cycles at T_a and T_{LN}, with the positive cycle as the final one. The area of the superconductivity transition of those characteristics tended to shift towards higher values of temperature, up to T_c=90,9K in measurement 13. The T_c increase always means the improvement of the superconductor quality. Further measurements (14 and 15) were carried out after treating the sample with different current cycles (at T_a and T_{LN}) during which current-voltage

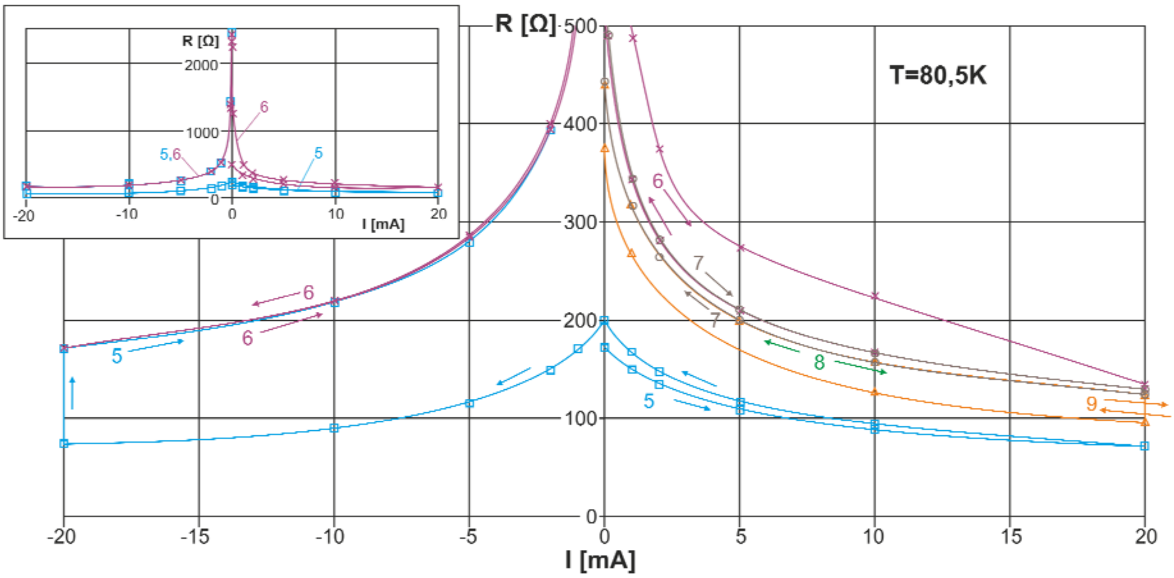

Fig. 2. Resistance characteristics of an HTS microbridge in the liquid nitrogen temperature under influence of a sequence of current cycles. The sequence of measurements corresponds with the numbers of curves and the direction of their arrows. In the insert – full 5 and 6 curves.

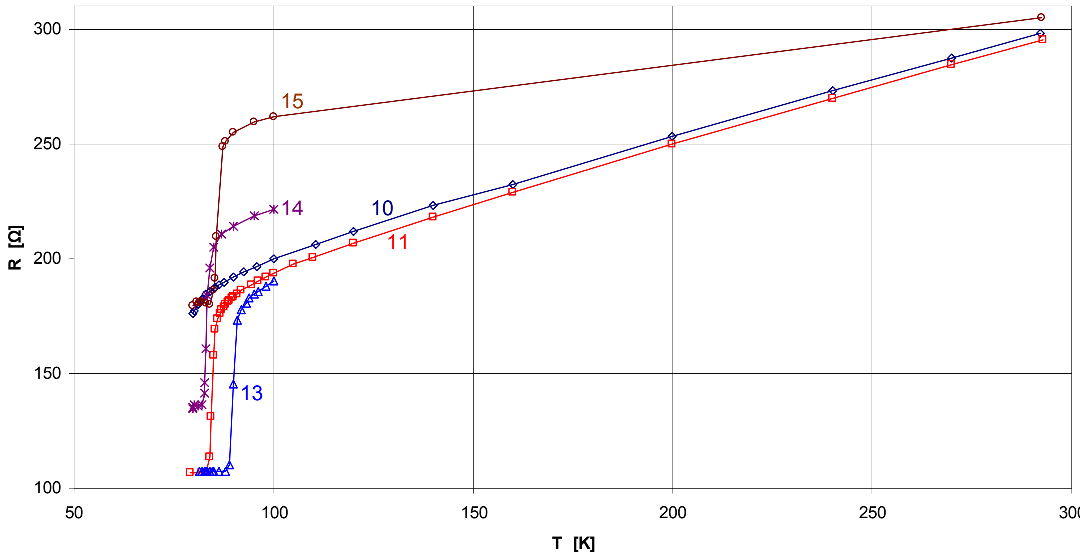

Fig. 3. Temperature dependences of the $YBa_2Cu_3O_{7-x}$ microbridge resistance. The numbers of curves correspond with the order of carried out measurements.

characteristics were determined. The final cycle was always the negative one. As the result, temperature characteristics tended to shift towards higher values of R, as if additional series resistances were affixed to the HTS microbridge circuit. The fact that both: the temperature width (ΔT_c) and the height of the superconductivity transition area ΔR_c, presented in Fig. 3, are basically identical (ΔT_c=1.3÷2K; ΔR_c=70÷74Ω), also proves the hypothesis.

Results analysis

In our previous research [11], it was not clearly established whether memory effect in the $Ag/YBa_2Cu_3O_{7-x}/Ag$ structure is unipolar or bipolar, which did not allow to determine the mechanism of this phenomenon. The results of the present research (Fig. 1 and 2) definitely prove that the resistance switching mechanism in an HTS microbridge is bipolar. Such examples of memory effects in materials of perovskite crystallographic structure are usually explained with the use of oxygen-ion O^{2-} electro-diffusion [5-8, 12-13]. Materials of this type have small activation energy of O^{2-} diffusion (0,7eV) [6, 14] and a great concentration of oxygen vacancies, which increases the probability of diffusion. Oxygen diffusion inside and outside the $YBa_2Cu_3O_{7-x}$ film changes the value of oxygen deficit *(x)*. Oxygen atoms play the role of acceptor dopant in some cell nodes. The increase of oxygen deficit causes reduction of charge carriers concentration (holes in high-temperature superconductors) and, as a consequence, resistance increase (this dependence is very strong as it is an exponential function [15]).

Thinking similarly to [5, 8], it can be assumed that in our HTS structure, in the areas of $YBa_2Cu_3O_{7-x}$, neighbouring the Ag electrodes, there are oxygen-depleted, so having a great resistance, layers. These layers are formed during a regular technological process of high-temperature superconductor production through oxygen thermo-diffusion into the environment [16]. If we supply electrodes with positive potential, high enough to provide O^{2-} ions with energy that exceeds the activation energy of diffusion (0,7eV), they will shift through oxygen vacancies towards the depleted layer, which will result in microbridge resistance decrease (R_L level). After switching off the voltage (current), oxygen ions will remain in new positions, so the R_L state will be stable. At the negative electrode polarization, oxygen ions are forced out of the layer neighbouring the electrode towards the inside of the HTS material. This leads to reconstructing the depleted layer and resistance increase up to the R_H level. The described mechanism explains the phenomenon of the HTS microbridge resistance switching between R_H and R_L stable levels, presented in Fig. 1 and 2.

The presence of the oxygen-depleted layer at the surface of the HTS means that a conductor/semiconductor junction appears, where the $YBa_2Cu_3O_{7-x}$ is the conductor and the oxygen-depleted layer of this material is the semiconductor [17]. Electrical conductivity of such junction is conditioned by a mechanism of space-charge-limited current [17 -19] with a parabolic dependence of current from voltage *($I \sim U^2$)*. Fig. 4 presents selected *I-U* characteristics, obtained during our measurements, in a double logarithmic scale.

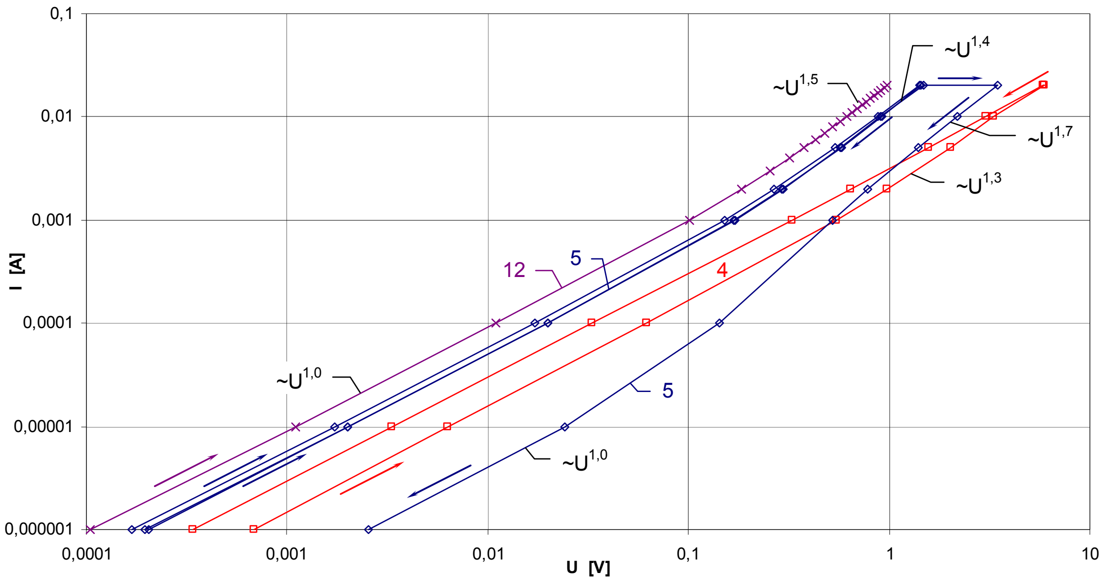

Fig. 4. Selected current-voltage characteristics of an HTS microbridge. The curves numbers correspond with Fig. 1 and 2. The arrows show the order of measurements (4 – when T=293K; 5,12 – when T=80.5K).

The initial fragments of those characteristics have *n*=1 slope coefficients, which proves that this is the ohmic-type of conductivity. However, at >100mV voltage, those coefficients equal 1.3 to 1.7, which suggests that a mixed mechanism with conductivity limited by space charge occurs here. The fragment of the greatest slop (*n*=1.7 in curve 5, Fig.4) corresponds with the branch of R_H high resistance in characteristics 5 from Fig. 2, which may be treated as confirmation of the depleted layer presence in the HTS microbridge at R_H state.

The process of oxygen ion diffusion explains also the shift of temperature characteristics in Fig. 3. O^{2-} ions in perovskite crystals may be placed not only in the nodes of the crystal lattice, but also out of them – in ion traps. Such traps are usually located in plane or space defects of the lattice. Ion activation energy of a trap is surely greater than the energy of O^{2-} diffusion process. Releasing ions from the traps and their diffusion through vacancies in the superconducting material cause the oxygen deficit decrease, which results in the increase of the superconductivity transition T_c [20, 21] in local areas. This results in characteristics shift: 10→11→13 in Fig.3, when the microbridge resistance in S state remains unchanged. The shift of characteristics 14 and 15 at the influence of negative current cycles is probably caused by forming additional oxygen-depleted layers or by enlarging the existing ones.

Summary

The results of experiments presented in this paper prove that the bipolar electro-resistance memory effect in a thin-film structure of $Ag/YBa_2Cu_3O_{7-x}/Ag$ occurs in liquid nitrogen and room temperatures. Processes of destruction and recovery of oxygen-depleted layers, existing nearby the electrodes and in the superconductor volume, may explain this phenomenon. The processes occur in O^{2-} ion electro-diffusion through numerous oxygen vacancies existing in a perovskite material.

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