

Oxygen index enhancement of epitaxial $YBa_2Cu_3O_{7-x}$ films due to VUV-irradiation

*A.A.Koz'ma, A.N.Stetsenko, T.I.Khramova, S.V.Malykhin, L.Z.Lubyany, B.I.Khrusch**

Kharkov State Polytechnical University, 21 Frunze St., 310002 Kharkiv, Ukraine

*Physico-Technical Institute for Low Temperature, National Academy of Sciences of Ukraine, 47 Lenin Ave., 310164 Kharkiv, Ukraine

Received April 4, 1996, revised version received February 11, 1997

Changes in structure and electrophysical properties of epitaxial $YBa_2Cu_3O_{7-x}$ films have been studied under air exposure and at VUV irradiation. After 4 hours irradiation, diffusion of oxygen into the film and improvement of superconductivity characteristics have been found. The superconducting transition (T_c> 77 K) has been revealed in the samples with tetragonal structure after 38 h. VUV-irradiation under a high partial oxygen pressure.

Исследованы изменения структуры и свойств эпитаксиальных пленок $YBa_2Cu_3O_{7-x}$ при выдержке в атмосферных условиях и при воздействии ВУФ-облучения. Облучение вакуумным ультрафиолетом в течение 4 ч. вызывает диффузию кислорода в пленку и улучшение ее сверхпроводящих характеристик. Для образцов с тетрагональной структурой обнаружен переход в сверхпороводяящее состояние при *T*> 77 К после 38 час. ВУФ-облучения в атмосфере с высоким парциальным давлением кислорода.

At present, coper oxide high-temperature superconductors (HTSC) $YBa_2Cu_3O_{7-x}$ are considered as the to be most prospective materials to be used as elements of high-sensitive micro- and nanoelectronic devices in the field of space materials science. The wide use of those materials is hindered, however, by their degradability.manifesting itself as irreversible changes in physical properties. In this work, effect of some factors acting in the outer space (OS) on the structure and properties of HTSC films has been studied by means of simulation of those factors in the earthly conditions.

Factors causing a degradation of 1–2–3 superconductors are of a great variety. Under atmospheric conditions, water vapor is known to give rise to the surface hydration and loosening. Therewith, the oxygen index becomes decreased in surface layers and the superconductive metal phase is transformed into a semiconductive one [1,2]. An exposure of HTSC in an oil-free vacuum for one day causes a substantial loss of the lattice oxygen, thus resulting in a significant deterioration of superconductivity [3].

When 1–2–3 HTSC are irradiated by electron, proton or ion beams, local structure inhomogeneities are formed as well as an amorphous surface layer, dielectric layers on interfaces between superconducting regions and crystal lattice defects. HTSC exposed in the OS are subjected to a specific influence, namely, an action of atomic oxygen at about 5 eV energy and an intense vacuum UV (VUV) irradiation (about 10 W/m^2 at $100<\lambda<200$ nm) is added to radiation and vacuum exposure under thermocycling conditions. Since it is just oxygen atomized by VUV radiation at a wavelength λ~150 nm that is the main component of the rarefied

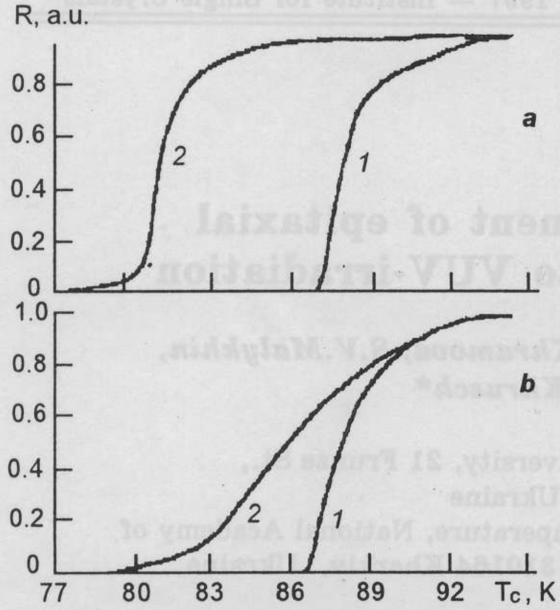

Fig.1. Resistive transition curves for epitaxial $YBa_2Cu_3O_{7-x}$ films stored under atmospheric conditions: a) films with misorientation less than 1° in the initial state (1) and after 2 years of exposure (2); b) the same for highly misoriented films (7 to 9°).

OS atmosphere, the degradation under OS conditions can be simulated to a great extent using a VUV radiation having a sufficient intensity in the region of oxygen atomization. The superconductivity degradation of 1–2–3 HTSC has been found to depend substantially on the initial state and the irradiation temperature [4,5]. In particular, single- crystalline 1–2–3 films turned out to be more radiation-resistant than polycrystalline samples [2,5].

The work is aimed at the study of structure and electrophysical properties variations of 1–2–3 films exposed to atmospheric conditions and to a VUV radiation.

About 200 nm thick epitaxial 1–2–3 films on single-crystalline $SrTiO_3$ substrates were used in experiments. The films were obtained by the layer-by-layer condensation of components in vacuum onto the substrates having the mosaic block misorientation (φ) no more than 0.5 deg. Y, BaF_2 and Cu layers were sputtered successively using independent sources at residual pressure 10^{-4} to 10^{-5} Pa. Copper and barium fluoride were evaporated using a resistive heater whole for yttrium, electron beam sputtering was using. The substrate temperature in the course of deposition was 573 K. The subsequent homogenizing anneal was performed in oxygen atmosphere in two stages: first, for 1 h at T=1123 K, and then at T=723 K for 0.5 h. According to the secondary ion mass-spectrometry data, the stoichiometric composition of films was constant within 1% for Y, within 0.25% for Ba and within 0.5% for Cu.

Critical characteristics of the superconducting transition were determined using the contact method from the temperature dependence of the electric resistance. Those characteristics are: the superconducting transition onset temperature, T_{co}, the zero resistance one, T_{cf}, and the transition width, ΔT_c. Using X-ray diffractometry, the phase composition and crystal lattice parameters (a, b, c) were determined. Unresolved (407) and (047) reflexes are typical for all films studied. This is caused by a rather small size of twinned microregions being in the range of 8 to 10 nm [6]. The macrodeformation level and oxygen index values $(7-x)$ were calculated according to the procedure described in [6] with account for the last above statement. VUV irradiation of samples was performed in a vacuum chamber under oxygen pressure $10-10^3$ hPa. The flux density was $J=10^{20}-10^{21}$ $m^{-2}s^{-1}$, or about 160 W/m^2 [8]. Radiation sources were distinct in energy dispersion characteristics (due to various windows materials used), apart from distinctions in integral flux ones. In particular, a great fraction of quanta had energy close to 10 eV in the second case. The irradiation was performed at T=300 K.

The samples under study were subdivided into two groups, depending on the heat treatment regime. For the first group (samples Nos. 1, 2, 3 and 5) the oxygen index after two annealing stages was 6.81 to 6.96, thus assuring the superconducting state occurring. Samples No.4 and 6 were subjected only to the first annealing stage. As a result, the film were saturated by oxygen insufficiently ($7-x$=6.62) and had no superconducting properties at T>77 K, but their conductivity was of a metallic character.

Freshly prepared samples 1 and 2 were characterized by a rather narrow superconducting transition curve (Table 1). Variations in the run of temperature dependences of electric resistance for sample 1 and 2 are presented in Fig.1. During the atmospheric exposure for 2 years, T_{cf} value was decreased to about 77–79 K. Therewith, T_{co} for samples with strong misorientations was changed insignificantly (88.9), the transition width being increased up to 6.6 K

Table 1.

Sample No	Additional treatment	T_{co}, K	T_{cf}, K	ΔT, K	c, Å	a, Å	7−x	φ, deg
1	initial state	89.5	86.5	1.5	11.661	3.867	6.85	<1
1	2 years exposure	82.6	77	5	11.668	3.865	6.81	<1
2	initial state	89.7	87	1.8	11.650	3.862	6.96	7–9
2	2 years exposure	88.9	79.5	6.6	11.668	3.869	6.78	7–9
3	initial state	87.5	79	5.5	11.659	3.867	6.84	<1
3	4 h VUV irradiation in air	86	82	2.5	11.656	3.864	6.88	<1
4	initial state	–	–	–	11.670	3.880	6.62	<1
4	4 h VUV irradiation in air	–	–	–	11.675	3.876	6.66	<1
5	initial state	82	77	3	11.668	3.865	6.81	<1
5	4 h VUV irradiation in oxygen atmosphere	89	82	4.5	11.669	3.865	6.82	<1
6	initial state	–	–	–	11.670	3.880	6.62	<1
6	38 h VUV irradiation in oxygen atmosphere	89	78	9	11.676	3.863	6.82	<1

(Fig.1, b), while for low-misoriented samples, the transition onset temperature was decreased to the same extent as T_{cf}, attaining the value of 82.6 K. For the same reason, the transition width remained essentially unchanged (Fig. 1a).

These data evidence that the degradation of a sample with small misorientations is unifirm through its volume, in contrast to highly misoriented sample. Changes in superconducting properties seem to occur in regions adjacent to blocks boundaries as well as to dislocations. Oxygen vacancies are assumed to be concentrated mainly in the same regions. The degradation is accompanied not only by dislocations depletion of oxygen, but also by their redistribution. An enhancement in the dislocation density was found accompanied by a broadening of the (00.13) line. In the sample 2, central regions of blocks retain their properties essentially unchanged, that is evidenced by invariability of T_{co} value (Fig.1, b). Such regions, however, are few in number so that the sample as a whole becomes deteriorated substantially, what temperature dependences have shown. The sample 1 in the initial state contains a smaller oxygen amount than the 2 one ($7-x$=6.85). Therefore, in spite of that the sample 2 loses substantially more oxygen in the course of degradation as compared to the 1 one [$\Delta(7-x)$=0.18 and 0.04, respectively], both oxygen indices become rather close after 2-year exposure (6.81 for 1 and 6.78 for 2), thus, final temperatures of semiconducting transition become equalized, too.

Temperature dependence of resistance for the sample 3 before and after the irradiation is presented in Fig.2, a. In the non-irradiated sample, that dependence is of a metallic character with the superconducting transition at 79 K. values of critical transition parameters (Table 1) point that the sample has relative low superconductivity characteristics. A VUV irradiation during several hours in air results in the formation of a dull layer on sample surface having a high resistance. A similar layer is formed after a prolonged (several months) air exposure of samples [9]. A shift of the temperature dependence of resistance, $R(T)$, and change of its slope were observed as a result of the VUV irradiation. After 30 min of the action, the T_{cf} value was shifted towards higher temperatures by 1.5 K, while after 4 h, the shift was increased up to 3 K. Therewith, the transition width was narrowed down to 2.5 K.

Dependences of T_{co} and T_{cf} on the irradiation time are shown in the inset of Fig.2, a. The process of superconducting properties enhancement as a function of the irradiation time has a damping character. Moreover, T_{co} and T_{cf} changes are not the same. While the final transition temperature increases monotonously, that of the transition onset first drops sharply by 2 K and then elevates somewhat. Therewith, the oxygen index (7−x) increases by 0.04 after 4-hour irradiation. This points to an increase of oxygen content in the 1−2−3 lat-

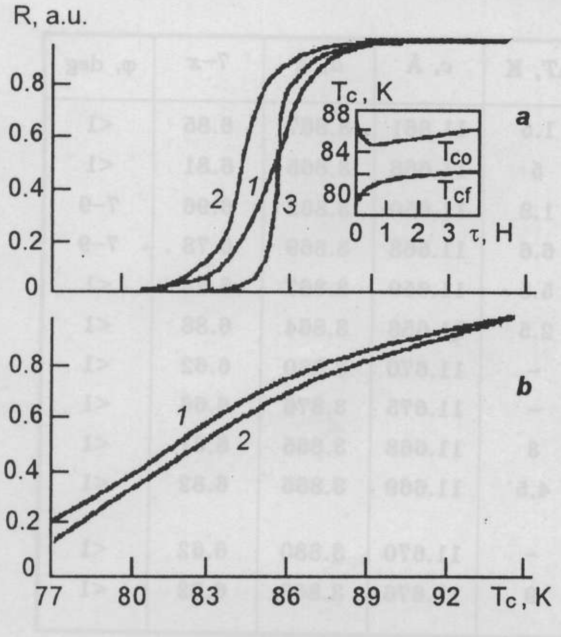

Fig.2. Resistive transition curves for epitaxial $YBa_2Cu_3O_{7-x}$ films at VUV irradiation in air: a) for films superconductive at T>77 K in the initial state (1), after irradiation for 30 min (2) and 4 h (3); b) for films having no superconductivity at T>77 K in the initial state (1), after 4 h of irradiation (2). Inset: T_{cf} and T_{co} variations as depending on the irradiation time for films (a).

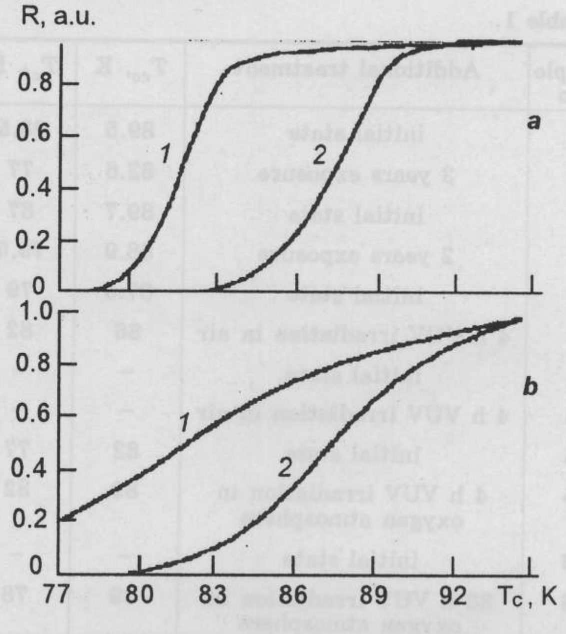

Fig.3. Resistive transition curves for epitaxial $YBa_2Cu_3O_{7-x}$ films at VUV irradiation in oxygen atmosphere: a) films superconductive at T>77 K in the initial state (1) and after 4 h of irradiation (2); b) films exhibiting no superconductivity at T>77 K in the initial state (1) and after 38 h of irradiation (2).

tice; but, if that increase would occur in a homogeneous manner, a monotonous elevation not only of T_{cf}, but also of T_{co} would take place. The revealed distinctions in changes of those temperatures can be explained, in our opinion, by that oxygen diffusion occurs in regions where the oxygen index is low. The existence of such regions in the form of interlayers adjacent to film grains boundaries is considered in [9]. The T_{co} lowering under irradiation may result from a degradation of regions with a higher oxygen content due to VUV-stimulated surface hydration causing a non-conducting layer formation.

To test the validity of that hypothesis, a non-superconducting sample No.4 was studied that can be considered as a material consisting mainly of the interlayers (Fig.2, b). Its lattice parameters and oxygen index correspond to the tetragonal phase (Table 1). When that sample is irradiated in the same conditions as the 3 one, the increase of the index ($7-x$) attains 0.04 as in the preceding case. However, no substantial changes of critical parameters occur, since a low oxygen index value is retained after irradiation (6.66). Moreover, similar to the sample 3, a surface non-conductive layer was observed to be formed which hinders the oxygen diffusion.

The irradiation of samples in a photolysis device in oxygen atmosphere was performed to attain a stimulated oxydation of 1-2-3 films. Superconductive and non-superconductive samples (5 and 6, respectively) were used similar to 3 and 4 ones. Temperature dependences of electric resistance for the sample 5 (analogue of 3) are presented in Fig.3, a. After 4 h of VUV irradiation, the $R(T)$ dependence shifts towards higher temperatures with a change of its slope. Therewith, the T_{co} becomes shifted by 7 K, the T_{cf} by 5 K, while the transition width increases from 3 K to 4.5 K (Table 1). The oxygen index value increases by 0.01. Since oxygen index of the initial sample was very close to HTSC characteristics deterioration, its small elevation (by 0.01) causes a significant shift of T_{co} and T_{cf} towards high temperatures.

The structure and properties of the sample 6 change most dramatically as a result of irradiation in oxygen atmosphere during 38 h. In the initial state, that sample had the tetragonal structure, the calculated oxygen index value was 6.62 (Table 1). Due to VUV irradiation, the oxygen index became ncreased up to 6.82, and the superconduc-ive transition was revealed. The $R(T)$ vari-ıtion character caused by the irradiation is hown in Fig.3,b. The transition onset takes lace at sufficiently high temperatures and emains almost unshifted in the course of rradiation. The transition width is 9 K, ınd superconductivity arises at T=78 K.

Thus, in this work, changes in oxygen ndex and superconductivity characteristics ıave been studied for 1-2-3 films exposed o atmospheric conditions for 2 years as vell as for those irradiated by VUV. For ıighly misoriented samples (7-9°), oxygen ndex and T_{cf} are found to decrease signifi-antly during the exposure while T_{co} hanges only slightly, thus evidencing an nhomogeneous run of degradation process. The atmospheric exposure of low-misori-ented samples results in an almost equal owering of T_{co} and T_{cf} at an insignificant lecrease of oxygen index (by 0.04), thus ɔointing that the sample degrades homoge-ıeously.

The VUV irradiation of superconductive samples with moderate critical parameters and low oxygen index causes an increase of he latter and an enhancement of supercon-ductivity characteristics. A more substan-tial elevation of T_{cf} has been observed for samples irradiated in oxygen atmosphere as compared to those irradiated in air, at a small oxygen index increase (0.01 to 0.04). It is found that a 1-2-3 film exhibiting no superconductivity at T>77 K can be saturated with oxygen in an amount sufficient to the superconductive transition by a prolonged VUV irradiation in oxygen atmosphere.

References

1. V.I.Nefedov, A.I.Sokolov, *Zh.Neorg.Khim.*, **34**, 2723 (1989).
2. E.A.Eremina, N.I.Oleynikov, V.I.Nefedov, *Zh. Vsesoyuzn.Khim.Obsch.*, *N4, (1989)*.
3. L.S.Palatnik, V.V.Prytkin, A.A.Koz'ma, in: Probl. of Nucl. Sci. and Techn. Ser. Nucl. Phys. Res. (Theory and Exper.), **4(12)th** Issue, Ukr. Phys. Techn. Inst. Publ., Kharkov (1990), p.72 [in Russian].
4. V.V.Kirsanov, N.N.Musin, in: Probl. of Nucl. Sci. and Techn. Ser. Nucl. Phys. Res. (Theory and Exper.), **1/2 (58/59)th** Issue, Ukr. Phys. Techn. Inst. Publ., Kharkov (1992), p.45 [in Russian].
5. A.A.Alekseenko, A.V.Bukalov, A.P.Galushka, *Sverkhprovodimost'*, **1**, 100 (1992).
6. A.A.Koz'ma, A.A.Nechitaylo, A.T.Pugachev, in: Abstr. of 3rd All-Union Conf. on Oxide Film Phys. (Petrozavodsk), Vol. 2, 21 (1991) [in Russian].
7. B.I.Khrusch, N.N.Agashkova, A.L.Antonenko, *Fiz.i Khim.Obrab.Mat.*, **5**, 67 (1975).
8. A.A.Koz'ma, S.V.Malykhin, L.P.Tischenko, *Fiz.i Khim.Obrab.Mat.*, **4**, 13 (1991).
9. L.S.Palatnik, V.N.Nikitsky, S.V.Ryabukha, *Sverkhprovodimost'*, **1**, 139 (1992).

Підвищення кисневого індексу епітаксіальних плівок $YBa_2Cu_3O_{7-x}$ за допомогою ВУФ-опромінення.

О.О.Козьма, О.М.Стеценко, Т.І.Храмова, С.В.Малихін, Л.З.Луб'яний, Б.І.Хрущ

Досліджено зміни структури і властивостей епітаксіальних плівок $YBa_2Cu_3O_{7-x}$ під впливом атмосферних умов та під дією ВУФ-опромінення. Опромінення вакуумним ультрафіолетом протягом 4 годин обумовлює дифузію кисню в плівку та підвищення її надпровідних характеристик. Для зразків з тетрагональною структурою виявлено перехід в надпровідний стан при T> 77 К після 38 год. ВУФ-опромінення в атмосфері з високим парціальним тиском кисню.