Technical Physics Letters, 2023, Vol. 49, No. 10

13.3;05.5

Study of the processes of formation of nanosized compounds in high-temperature superconductor materials upon implantation of Ba^+ ions

© D.A. Tashmukhamedova, A.N. Urokov

Tashkent State Technical University, Tashkent, Uzbekistan
E-mail: ftmet@mail.ru

Received September 19, 2022
Revised July 27, 2023
Accepted September 2, 2023

In this work, we have studied for the first time the effect of Ba ions implantation on the $CuOY_2O_3BaO$ ceramics composition and band gap E_g, as well as on the number of valence electrons, by using the methods of Auger electron spectroscopy and spectroscopy of characteristic electron energy losses and by measuring energy dependences of secondary electron emission coefficient σ. It is shown that, after ion implantation, the value of σ increases in the entire investigated range of primary electron energy E_p. This increase is practically independent of the substrate temperature in the range $T = 85-300$ K. Band gap E_g increases from 0.5 to 4.5 eV, which is explained by the formation of a thin ($\sim 40-50$ Å) layer enriched with barium oxide.

Keywords: ion implantation, band gap, secondary electron emission coefficient, Auger spectrum, superconducting properties, ceramics.

DOI: 10.61011/TPL.2023.10.57061.19370

At present there are conducted intensive investigations devoted to creating new types of high-temperature superconductors (HTSC) [1–7] and to studying the effect of various external impacts on their properties [8–13]. Paper [3] shows that irradiation with ^{60}Co γ-photons of ceramic HTSC materials Bi(Pb)-2223 with different oxygen contents results in non-monotonic dependence of critical temperature T_c on the radiation dose at fluences below $2 \cdot 10^{18}\,\mathrm{cm}^{-2}$. At fluences above $> 2 \cdot 10^{18}\,\mathrm{cm}^{-2}$, the character of the T_c and specific resistance ρ dependences is independent of the thermal pretreatment, which may indicate that the radiation-damage mechanism is one and the same for materials with excess and deficient oxygen.

Mikhailov et al. [7] have proposed a method for obtaining new superconducting composite materials based on HTSC compounds with enhanced current-carrying capability in both the zero magnetic field and high-strength external magnetic fields. Of especial interest is obtaining of a second-generation HTSC tape [8]. These electrotechnical materials are being created based on epitaxial heterostructures and are very promising in developing novel electric-power devices.

In the course of operation, HTSC materials may be exposed to external impacts of various types: heating, long-term storage in air, bombarding with electrons or ions, irradiation with photons, etc. Therefore, it seems very important to develop a technique allowing retention of stability of those materials' properties under different exposures. For instance, during recent years there were proposed possible versions of solving the problems typical of the Lunar Program by using devices involving elements of high-temperature superconductivity technology [12]. Earlier we have comprehensively studied the effect of low-energy ion implantation on the composition and electronic structure of different-nature materials [14–18]. Results of such investigations for HTSC materials are still unavailable.

This paper presents for the first time experimental data on the effect of low-energy Ba^+ ion implantation on the composition, band energy parameters and emission characteristics of the $CuOY_2O_3BaO$ ceramics.

The implantation was performed using Ba^+ ions with energies of 0.5 to 5 keV at the saturation fluence of $D = D_{sat} = (6-8) \cdot 10^{16}\,\mathrm{cm}^{-2}$. As the barium source, barium titanate (BaTi) pellets were used. Heating of a quartz tube filled with BaTi pellets produced barium vapors, a portion of which gets ionized after falling on the surface of incandescent tungsten coil. The main part of investigation was performed at $E_0 = 0.5$ keV.

All the technological processing procedures, as well as surface investigation, were performed at one and the same setup (of the USU-2 type) in vacuum of $P \leqslant 10^{-7}$ Pa. Composition and electronic characteristics of the material surfaces were studied by Auger electron spectroscopy (AES) and spectroscopy of characteristic electron energy losses (SCEEL), and also by measuring energy dependences of secondary electron emission coefficient σ and photoelectron quantum yield. In the experiments, an Auger spectrometer equipped with a small-angle Yuza–Rozhansky analyzer was used. The Auger spectrometer sensitivity to impurities was $0.05-0.1\%$. The total error in determining the Auger peak positions in the spectrum did not exceed $0.8-1$ eV. The AES analysis depth was $\sim 5-10$ Å. Energy positions of SCEEL peaks and those of elastically reflected electrons were determined accurately to $2-3\%$.

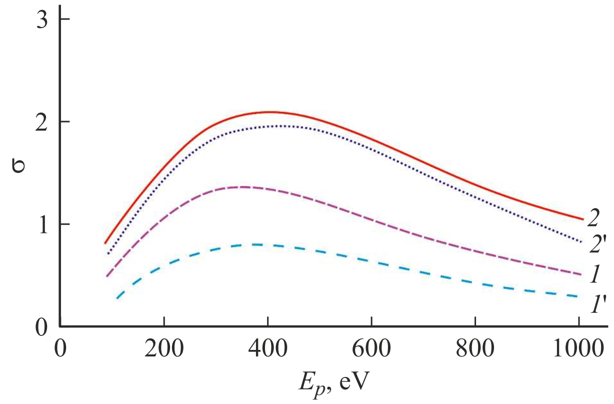

Figure 1. Dependences $\sigma(E_p)$ for the unimplanted HTSC (*1*, *1'*) and HTSC implanted with Ba^+ ions (*2*, *2'*). T, K: *1*, *2* — 300, *1'*, *2'* — 85.

The photon-energy dependence of intensity I of light passing through the sample (transmission coefficient K) was measured by using spectrophotometer UV-1280. The impurity depth profile was obtained by the layer-by-layer Auger analysis with sputtering the sample surface by 3 keV Ar^+ ions at the incidence angle of $\sim 85^\circ$ relative to the normal; etching rate was $\sim 5 \pm 1$ Å/min. The error in determining the atomic concentration was $\sim 5-8$ at.%.

The HTSC surface state was analyzed in two temperature modes: at room temperature ($T \approx 300$ K) and at the liquid nitrogen boiling point ($T \approx 80-85$ K) which is close to the $CuOY_2O_3BaO$ critical temperature ($T_c = 85$ K, $\Delta T = 1.5$ K). It is known that the secondary electron emission coefficient is highly sensitive to variations in the surface composition and structure. Fig. 1 presents the σ dependence on primary electron energy E_p for $CuOY_2O_3BaO$ implanted by Ba^+ ions with $E_0 = 0.5$ keV at saturation fluence $D = 6 \cdot 10^{16}$ cm^{-2}. One can see that after ion implantation the value of σ increases in the entire considered range of primary electron energy E_p. Notice that σ values of the unimplanted HTSC measured at room temperature ($T = 300$ K) and at the critical temperature ($T_c = 85$ K) are drastically different.

Apparently, emission efficiency of HTSC materials in the superconducting state (at $T = 80-85$ K) becomed significantly lower. We observed a similar effect in the case of photoelectron emission. Values of the σ coefficient of the ion-implanted HTSC, which were measured at $T = 300$ K and $T_c = 85$ K, differ from each other only slightly. Probably, ion implantation shifts T_c towards lower temperatures. However, studies of superconducting properties of materials by using magnetic fields have shown that the T value of ceramics after implanting Ba^+ ions with $E_0 \leqslant 3$ keV remains almost the same. To clarify this point, we studied variations in the composition of near-surface layers of the ion-implanted HTSC by using AES combined with ion etching. The analysis showed that embedding Ba into the near-surface layer induces redistribution of atoms in the ion-implanted layer. In order to determine the modified layer thickness, we first measured the depth profile of intensity of the high-energy barium peak (584 eV) for the unimplanted and ion-implanted HTSC materials. Fig. 2 shows that after ion implantation the Ba concentration gets increased in the near-surface region up to 30–40 Å thick. In deeper layers, the HTSC composition remains almost unvaried. Therefore, superconducting properties of $CuOY_2O_3BaO$ may be assumed to be of a more bulky character than emission properties. It is worth noticing that, as a result of ion implantation, compounds like BaO and Ba_2O are mainly formed. The conditional composition of the ion-implanted HTSC surface is as follows: $CuO_{0.5}Y_{0.5}OBa_3O_2$. Concurrently with AES measurements, SCEEL-evaluation of number n_{av} of valence electrons per HTSC molecule was performed (Table 1).

Fig. 3 presents dependences of the intensity of light passing through the sample (light absorption spectroscopy) for HTSCs obtained prior to and after ion implantation. One can see that the $I(h\nu)$ curves are stepwise: first, up to a certain $h\nu$ value, intensity I does not change (i.e. no light absorption occurs), and then drops sharply to zero. In the unimplanted HTSC, intensity I does not vary up to $h\nu = 4$ eV. It is possible to assume that in this range of $h\nu$ the light reflection coefficient R is ~ 0.32, transmission coefficient is $T \sim 0.68$, and absorption coefficient is zero. In the case of the HTSC implanted by Ba^+ ions, intensity I remains virtually constant up to $h\nu = 0.4$ eV, and coefficients are $R = 0.23$, $T = 0.77$, $K = 0$. Extrapolation of the sharply reducing part of the curve to the $h\nu$ axis provides an approximate value of band gap E_g. Evidently, E_g for the unimplanted ceramics is 0.5 eV, while that for the ion-implanted ceramics is 4.5 eV. The

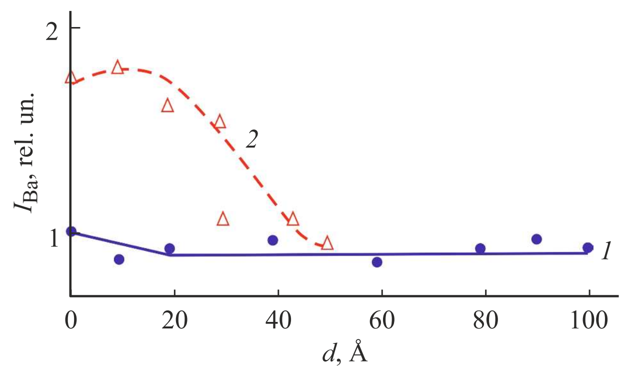

Figure 2. Depth profile of the Ba Auger peak intensity for the unimplanted sample (*1*) and HTSC sample implanted by Ba^+ ions with $E_0 = 0.5$ keV, $D = 6 \cdot 10^{16}$ cm^{-2} (*2*).

Table 1. Band gap width and average number of valence electrons

Material	E_g, eV	n_{av}	R	T	K
$CuOY_2O_3BaO$	0.5	4	0.32	0.68	0
$Ba^+ \to CuOY_2O_3BaO$	4.5	3.5	0.23	0.77	0

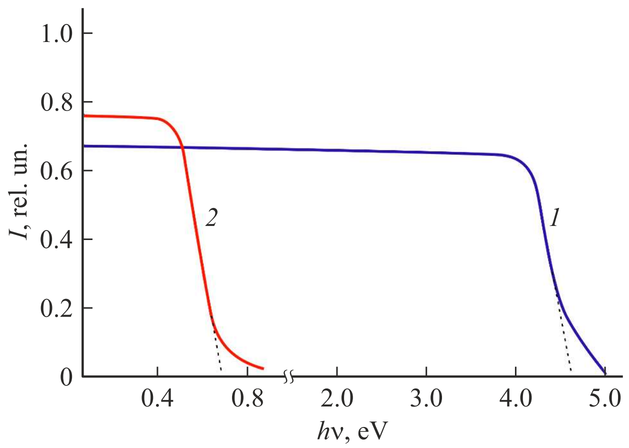

Figure 3. Photon-energy dependence of intensity of light passing through the HTSC prior to (*1*) and after implanting Ba^+ ions with $E_0 = 0.5$ keV and $D = 6 \cdot 10^{16}$ cm^{-2} (*2*).

Table 2. Atomic concentrations of different elements on the HTSC surface

Material	C, at.% ($\Delta C = \pm 5\%$)			
	Cu	O	Y	Ba
$CuOY_2O_3BaO$	12	50	25	13
$Ba^+ \rightarrow CuOY_2O_3BaO$	8	35	17	40

values of band gap and average number of valence electrons n_{av} are listed in Table 1.

When the unimplanted HTSC is in the superconducting state, its Fermi level is located in the vicinity of the upper edge of the filled states. Between the filled and free states there is a narrow gap with the energy width of 0.4–0.5 eV. As for the ion-implanted $CuOY_2O_3BaO$ samples, an increase in the barium oxide concentration and arising of free metal atoms result in the loss of sample surface superconducting properties even at the liquid-nitrogen temperature. Along with this, superconducting properties in deeper layers of the sample ($d \geqslant 50-60$ Å) remain fully preserved. After ion implantation, electronic structure of the superconductor surface becomes characteristic of thin oxide films.

Table 2 presents the approximate atomic concentrations of different elements on the $CuOY_2O_3BaO$ surface prior to and after implanting Ba^+ ions at $E_0 = 0.5$ keV and $D = 6 \cdot 10^{16}$ cm^{-2}. The table shows that ion implantation induces redistribution of the HTSC material atoms in the near-surface region. Ion implantation provides a three-fold increase in the Ba concentration, while concentrations of other HTSC components decrease by 1.5-1.6 times.

Thus, the paper demonstrates that implantation of Ba^+ ions with $E_0 = 0.5$ keV induces formation in the $CuOY_2O_3BaO$ near-surface region of a thin ($\sim 40-50$ Å) layer enriched with barium. It has been established that, after ion implantation, superconducting properties in the ion-implanted layer get lost at $d = 50-60$ Å and remain preserved at $d \geqslant 60-70$ Å. Approximate surface composition of the ion-implanted HTSC $CuO_{0.5}Y_{0.5}OBa_3O_2$ has been determined for the first time; the band gap, average number of valence electrons, and optical parameters of the unimplanted and implanted HTSC materials have been evaluated.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] D.V. Masterov, S.A. Pavlov, A.E. Parafin, Yu.N. Drozdov, Tech. Phys., **52** (10), 1351 (2007). DOI: 10.1134/S1063784207100167.

[2] R.-Z. Cao, L.-J. Zhang, L.-Y. Ding, X.-P. Liu, X.-Y. Liu, P. Jin, S.-T. Liu, H.-Ch. Tao, Comput. Mater. Sci., **7**, 111558 (2022). DOI: 10.1016/j.commatsci.2022.111558

[3] V.A. Gurinovich, F.P. Korshunov, V.K. Shesholko, Dokl. BGUIR, № 1 (9), 69 (2005). https://libeldoc.bsuir.by/handle/123456789/30832 (in Russian)

[4] Y. Zhang, X. Xu, Physica C, **595**, 1354031 (2022). DOI: 10.1016/j.physc.2022.1354031

[5] A.V. Varlashkin, B.I. Massalimov, V.P. Martovitsky, Bull. Lebedev Phys. Inst., **45** (4), 99 (2018). DOI: 10.3103/S1068335618040012.

[6] A. Kujur, D. Behera, J. Magn. Magn. Mater., **377** (3), 34 (2015). DOI: 10.1016/j.jmmm.2014.10.004

[7] B.P. Mikhailov, I.A. Rudaev, A.V. Bochko, V.F. Shamray, A.B. Mikhailova, B.V. Spitsin, *Sverkhprovodyashchy kompozitsionny material na osnove VTSP-soedineniy i sposob ego polucheniya*, patent RF, bul. № 24 (2012). (in Russian)

[8] S.S. Kostinsky, Problemy energetiki, **20** (1-2), 14 (2018). DOI: 10.30724/1998-9903-2018-20-1-2-14-32 (in Russian)

[9] S.M. Anlage, J. Opt., **13** (2), 024001 (2011). DOI: 10.1088/2040-8978/13/2/024001

[10] S.Kh. Gadzhimagomedov, D.K. Palchaev, Zh.Kh. Murlieva, G.Sh. Shapiev, R.M. Emirov, N.M.-R. Alikhanov, F.F. Orudzhev, M.Kh. Gadzhiev, P.M. Saypulaev, A.E. Rabadanova, Vestn. Dagestan. gos. un-ta, **35** (4), 79 (2020). DOI: 10.21779/2542-0321-2020-35-4-79-89 (in Russian)

[11] A.E. Shchukin, A.R. Kaul, A.L. Vasiliev, I.A. Rudnev, Kondensirovannye sredy i mezhfaznye granitsy, **23** (1), 122 (2021). DOI: 10.17308/kcmf.2021.23/3313 (in Russian)

[12] V.A. Maevsky, V.V. Aseev, A.S. Ivlev, N.A. Nizhelsky, M.A. Sysoev, V.V. Sinyavsky, Kosmicheskaya tekhnika i tekhnologiya, № 2 (25), 14 (2019). (in Russian) DOI: 10.33950/spacetech-2308-7625-2019-2-14-27

[13] B.A. Belyaev, I.V. Govorun, A.A. Leksikov, A.M. Serzhantov, Tech. Phys. Lett., **38** (3), 211 (2012). DOI: 10.1134/S1063785012030066.

[14] D.A. Tashmukhamedova, B.E. Umirzakov, M.A. Mirzhalilova, Izv. RAN. Ser. fiz., **68** (3), 424 (2004). https://www.elibrary.ru/item.asp?id=17641066 (in Russian)

[15] Kh.Kh. Boltaev, D.A. Tashmukhamedova, B.E. Umirzakov, J. Surf. Investig., **8** (2), 326 (2014). DOI: 10.1134/S1027451014010108.

[16] D.A. Tashmukhamedova, Izv. RAN. Ser. fiz., **70** (8), 1230 (2006). https://elibrary.ru/item.asp?id=9296378 (in Russian)
[17] B.E. Umirzakov, J.Sh. Sodikjanov, D.A. Tashmukhamedova, A.A. Abduvayitov, E.A. Rabbimov, Tech. Phys. Lett., **47**, 620 (2021). DOI: 10.1134/S1063785021060262.
[18] D.A. Tashmukhamedova, M.B. Yusupjanova, J. Surf. Investig., **15** (5), 1054 (2021). DOI: 10.1134/S1027451021050402.

Translated by Solonitsyna Anna