

The electrical conductivity of the surface layers of oxide polycrystalline semiconductors irradiated by accelerated ions

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Abstract. The effect of ion irradiation on the electrical conductivity of low resistance and high resistance subsurface layers of polycrystalline Li-Ti ferrites is studied. Irradiation was carried out with accelerated Ar⁺ ions with energy E=150 keV and the fluence $F = 10^{16}$ ions/cm². It is found that exposure of high-resistance ferrites significantly decreases the activation energy E_{σ} and considerably increases the electrical conductivity of the surface layers. The effect of the ion beam on the stated low-resistance characteristics of the samples is much weaker. The observed decrease in the numerical values of E_{σ} is due to the decrease in the values of the intergranular potential barrier caused by the exposure. The decrease in the potential barrier difference is due to the decreased degree of the grain boundary oxidation which is caused by preferential desorption of oxygen under the action of the ion beam. The thermal stability of the electrical characteristics of the investigated ferrites subjected to ion radiation-induced modification is determined.

1. Introduction

In [1–3], it is shown that exposure to accelerated ions of a broad class of ionic oxide dielectrics (crystals of magnesium, quartz and lithium niobate oxides, as well as various types of electric-grade ceramics) causes a huge increase in the electrical conductivity of the surface layers. The maximum effect (more than 9 orders of magnitude) is achieved in irradiation with the fluence $F = (10^{16} - 5 \times 10^{16})$ ions/cm². Transition of the high-resistance dielectric surface from an insulating state to a conducting one is followed by a sharp decrease in the activation energy from 1.5 eV to several hundredths of eV, which indicates the change of the conduction mechanism. The observed effect is fundamental and virtually does not depend on the nature of the accelerated ions. The analysis of the obtained results together with the data characterizing the structural state of the implanted layers suggests that distortion of the stoichiometry of the dielectric material surface caused by the preferential oxygen desorption under ion bombardment determines the formation of the resistive state [1]. It can be argued that the ion irradiation technique to modify the electrical conductivity can be extremely promising with respect to a sufficiently wide class of virtually significant oxide polycrystalline semiconductors. The considerations are based on the following assumptions. The most characteristic feature of oxides, as a special class of semiconductors, is significant deviations from the



stoichiometric ratio of metal and oxygen ions. As a result, electrically active centers, donors or acceptors, are formed in the crystal lattice of oxides. The concentration of the centers depends on temperature, the nature of the gaseous medium, and other process factors. Structures with important practical properties can be created by shifting the stoichiometry of the metal-oxygen ratio. In this regard, testing of new and innovative techniques to produce an energy impact on this class of materials can help to solve this kind of problems.

The research aims to find out the nature and effectiveness of ion-irradiation impact on the conductivity of the oxide polycrystalline semiconductor surface layers, a sufficiently large group of spinel-type ceramic among them.

2. Experimental procedure

The object to be studied was ferrite lithium-titanium ceramic, which can be referred to this class of materials. The ceramics was made using ceramic technology ($T_s = 1280$ K, the sintering time was 2 hours) from a mechanical mixture of Li_2CO_3 -11.2%, MnO -2.7%, TiO_2 -18.65%, ZnO -7.6%, Fe_2O_3 -59.81% composition (by wt.%). Its chemical composition was $\text{Li}_{0.649}\text{Fe}_{1.598}\text{Ti}_{0.5}\text{Zn}_{0.2}\text{Mn}_{0.051}\text{O}_4$. The samples were made in the form of pellets of 15 mm diameter and 1.5 mm thick. Due to the heterogeneity of ceramics oxidation in sintering, the nonuniform depth distribution of the electrical conductivity and its activation energy in the thin surface layers were normally of the order of 200–300 μm . The nonuniform layers formed in sintering were removed by mechanical sanding. The samples with uniform depth distribution of the electrical characteristics were tested. The samples were irradiated with accelerated Ar ions, the energy $E = 150$ keV, the fluence $F = 10^{16}$ ions/ cm^2 using the ion-beam setup "Vesuvius 5M". The temperature in irradiation did not exceed 400 K. The static electrical conductivity was measured in the temperature range of (300–600) K with two-probe spreading resistance technique [4] to determine the resistance of the thin layers.

3. Experimental results

Two types of specifically prepared samples with different initial values of the electrical conductivity and electromigration activation energy were tested. The temperature dependences for the electrical conductivity are shown in Figures 1 and 2.

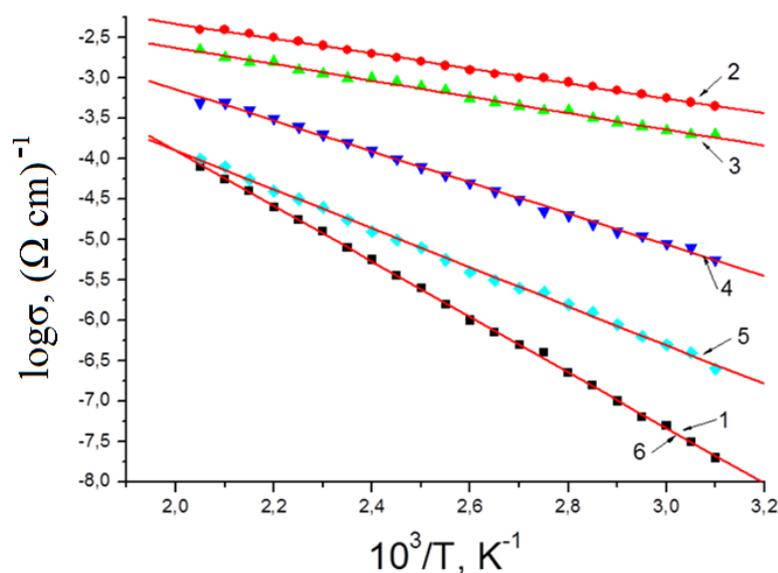


Figure 1. Temperature dependences of electrical conductivity for A-type ferrite ceramics before ion irradiation (Curve 1), after ion irradiation (Curve 2). Curves 3–6 are for temperature dependences after annealing of the irradiated sample at $T = 540, 570, 590,$ and 630 K, respectively.

The first A type, high-resistance samples ($\rho \approx 4.5 \cdot 10^6$ Ohm-cm at $T = 360$ K), indicated an increased and uniform value $E\sigma = 0.68$ eV throughout the depth. The second B type, low-resistance samples ($\rho \approx 4 \cdot 10^3$ Ohm-cm at $T = 360$ K), according to the data obtained by electrophysical measurements, showed low activation energy of conduction $E\sigma = 0.22$ eV.

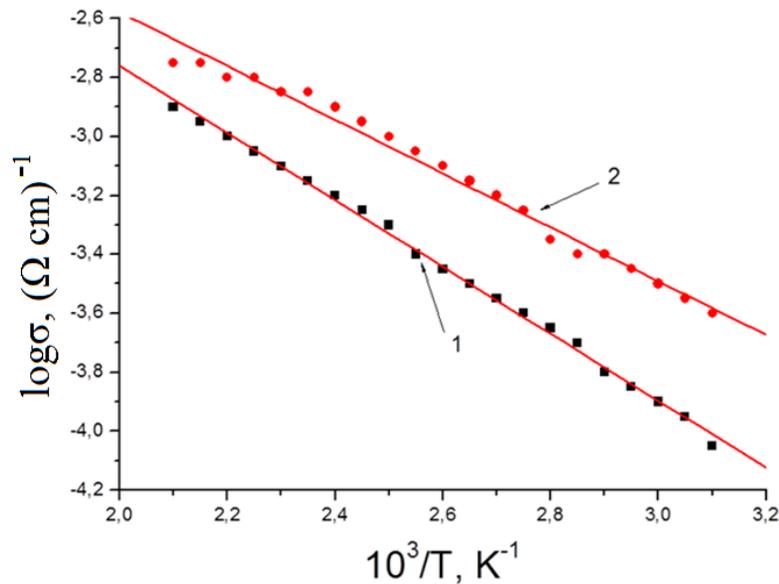


Figure 2. Temperature dependences of the electrical conductivity for B-type ferrite ceramics before ion irradiation (Curve 1), after (Curve 2) ion irradiation.

Activation energy $E\sigma$ is an essential characteristic of the electromigration in the matter. In contrast to single crystals in polycrystalline oxide semiconductors, which are an inhomogeneous conducting medium, the activation energy of electromigration is strongly affected by the grain boundaries (GB). As is well known, in heterogeneous structures, a potential barrier occurs at the grain boundaries. This barrier is caused by the excessive content of acceptors in GB, compared to the amount of the grain volume. When electrons are trapped by acceptors, the concentration of charge carriers decreases and a negative surface charge occurs, which causes increase in the electrostatic potential at the grain boundary. Oxygen atoms can be considered the most probable acceptors. In sintering of ferrite, oxidation-reduction reactions actively proceed and affect the boundary properties. Due to higher diffusion permeability, GBs are actively enriched with oxygen [5]. As a result, it becomes more oxidized; this causes decrease in Fe^{+2} ion concentration in its vicinity, and hence, charge carrier concentration.

The impact of potential barriers on electric charge transfer in heterogeneous structures is manifested through the mobility of charge carriers, which, as reported in [6], can be described by the expression:

$$\mu_n = \mu_s \mu_b (\mu_s + \mu_b)^{-1}, \quad (1)$$

where μ_s , μ_g , μ_b are the mobility in polycrystalline semiconductors, grains and barrier mobility, respectively. At this, $\mu_b = AT^{-1} d_g \exp(-\varphi_b/kT)$, where φ_b is the potential barrier difference, A is the constant, d_g is an average grain size.

Theoretically, the connection between the potential barrier at the grain boundaries and the conductivity is considered in [7], where the potential barrier height is determined by the relation:

$$\varphi_b = F_1 - F_2 = kT \ln n_1/n_2, \quad (2)$$

where F_1 and F_2 are Fermi energies; n_1 and n_2 are charge carrier concentrations. Indices 1 and 2 are the volume and boundary of the crystallite, respectively.

It is obvious, that μ_s value will be defined by the smallest mobility value. If $\mu_s \gg \mu_b$, then $\mu_g \approx \mu_b$. Typically, at relatively low temperatures, the barrier mobility is much lower than the intragranular one. Under these conditions, the activation growth of the ferrite ceramic electric conductivity with temperature will be determined by the potential barrier difference. The studies of the static conductivity of the Li-Ti ferrite ceramics in the temperature range of (350–500) K reported in [8] are fully consistent with these considerations.

Thus, it can be argued that the difference in the activation energy of conduction for the two tested types of ceramic samples is caused by the difference in GB oxidation. The more oxidized GB, the greater is the potential barrier difference, and hence the activation energy of conduction. In light of this understanding, we analyze the data on the effect of radiation treatment on the parameters of the electromigration in the ferrite ceramic. For the general case, the change in the value of the intergranular potential barrier under irradiation may be due to ionization processes in ceramics, which are not followed by change in its composition, and due to the oxygen exchange with the environment. In the latter case, the stoichiometric metal ion-oxygen ion ratio changes.

First, we conducted test experiments to study the effect of gamma rays irradiation with radioactive ^{60}Co isotope. The exposure dose was 10^6 – 10^7 r-units. This type of radiation initiates ionization processes and creation of atomic displacements by secondary electrons in the crystal lattice. No significant change in the conductivity and activation energy of conductivity was observed within these doses. Consequently, these processes cannot lead to the change in the GB state and the value of the intergranular potential barrier. Figures 1 (Curve 2) and 2 (Curve 2) show the temperature dependences of the electrical conductivity for the samples after irradiation with accelerated Ar^+ ions. Table 1 shows the values of the activation energy E_σ which characterizes the electromigration in the ion-modified layers of ferrite.

Table 1. Effect of ion irradiation and subsequent thermal annealing on the value of the activation energy of the electrical conductivity in the ferrite surface layers

Ceramics type	E_σ , eV					
	before irradiation	after irradiation	after annealing of the irradiated ceramics			
			T=540 K	T=570 K	T=590 K	T=630 K
A	0.68	0.18	0.19	0.32	0.49	0.68
B	0.22	0.19	-	-	-	-

The obtained results indicate that irradiation of the high-resistance ferrite with ions causes a significant decrease in the activation energy of the electrical conductivity and increases the conductivity of the modified layers. The action of the ion beam on the low-resistance samples is much weaker. At this, the activation energies of the conductivity for both ionirradiated low-resistance and high-resistance ferrite samples are found to be virtually identical. The obtained results show that ion irradiation can cause decrease in the potential barrier difference in the surface layers of lithium-titanium ferrite ceramics.

In the experiment, the sample irradiation was performed with accelerated ions in vacuum, the oxygen pressure being decreased. The temperature of the samples did not exceed $T = 400$ K due to radiative heating. The control experiments showed that thermal annealing of the ferrite samples in vacuum at this temperature had no significant effect on their electrical conductivity and E_σ value. Hence, its change after ion irradiation with these parameters is of purely radiative nature.

It is known that in interaction of ion beams with multi-component materials preferential sputtering of one of the components occurs. Bombardment of the oxide material surface with accelerated ions and the cascade processes developing therein lead to breakage of the bonds between oxygen and metal ions and preferential desorption of oxygen, its partial pressure being low, and cause stoichiometric deviation. This process should be especially efficient in the weakened areas of ceramics, grain boundaries in particular. When oxygen atoms escape, the valence balance is achieved by transition of the part of iron ions localized in GB from a threevalence charge state to a bivalent one. The decreased excess concentration of oxygen ions in the region of the grain boundary caused by ion bombardment reduces the potential barrier difference, and therefore, it decreases the activation energy of electromigration. These considerations are in agreement with the data obtained for the effect of oxidative annealing on the conductivity of the ion-modified layers.

The experiments showed that the initial electrical conductivity of the irradiated ferrites can easily be recovered by thermal annealing in air. Annealing was carried out in cyclic heating. The hold time at a fixed temperature was 10 minutes. The study showed that oxidizing annealing at $T < 540$ K has no effect on the conductivity of the modified layers. As can be seen from the data shown in Figure 1, with further increase in temperature in a sufficiently narrow range of $T=(570-630)$ K, the electrical conductivity of the irradiated sample decreased to the values corresponding to those of the unirradiated one. The decrease in the conductivity due to thermal annealing is attended by an increase of the activation energy of electromigration (Table 1).

The described behavior of the conductivity in the ion beam-modified polycrystalline ferrites in annealing in air can be satisfactorily explained by oxidation due to chemisorption on the atmospheric oxygen surface and its diffusion to grain boundaries [9, 10]. Thus the original oxidation state of GB and potential barrier difference recover.

In conclusion, practical perspectives of the obtained results should be emphasized. A number of elements of electronic devices, which are widely used in practice, were developed based on the barrier effects in polycrystalline oxide semiconductors, [11]. They are, in particular, different types of thermistors, posistors and varistors. The results of the study show that ionbeam processing, in principle, can be successfully used as a new effective tool for effective control of the potential barrier difference.

4. Conclusions

1. Irradiation of the polycrystalline ferrite by accelerated ions of an inert argo gas causes changes in the electrical conductivity and the activation energy of the electromigration defined by the potential barrier difference. This can be attributed to activation of regenerative processes due to preferential sputtering of oxygen from GB by accelerated ion beams.

2. The electrical characteristics of the surface layers of polycrystalline ferrites subjected to ion radiation-induced modification do not depend on temperature and remain stable in heating the samples in air in the temperature range of $T = (300-520)$ K.

3. In thermal annealing of the irradiated samples in the temperature range of $T = (540-630)$ K, the original state of the material completely recovers. This occurs due to the oxidative process caused by chemisorption on the surface of the atmospheric oxygen and its diffusion to the region of grain boundaries.

Acknowledgements

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