

Effect of ion-plasma treatment on oxidation–reduction processes in lithium–titanium-zinc ferrites

A P Surzhikov¹, E N Lysenko¹, S A Gyngazov¹, T S Frangulyan¹, S A Lamonova¹

¹National Research Tomsk Polytechnic University, 30 Lenin Ave, 634050, Tomsk, Russia

E-mail: lysenkoen@tpu.ru

Abstract. We examined the effect of nitrogen, oxygen and argon plasma on the diffusion-controlled oxidation-reduction processes in lithium-titanium-zinc ferrite ceramics by measuring the activation energy of electrical conductivity in the depth of the sample. The experimental results show that the high-temperature treatment in polycrystalline ferrites by nitrogen or argon ion plasma greatly accelerates the oxidation-reduction processes in ferrites and changes the process direction depending on the partial pressure of oxygen.

1. Introduction

Recently, the radiation effect methods have been used to exert the effective effect on the structural condition and different physical-mechanical properties of a wide range of materials [1-5]. A particular interest has been shown in research on the modification of the surface and near-surface layers of materials based on oxide compounds in order to develop new a new optical, mechanical, electro-physical and chemical properties. [6-7]. This is due to the need to resolve a number of practical problems, such as the creation of conductive surface layers on non-metallic substrates, creation of surface layers with high adhesion and strength properties, etc.

As regards the efficiency of the effect on the surface condition, the methods of ion plasma treatment occupy one of the leading positions. By varying the parameters of the electric discharge forming plasma, as well as the type of gas it is possible to control the nature of that impact. In view of this, the applications of ionic technology methods as a means aimed at changing the properties of solids were very diverse.

The basic factor combining the ion plasma processes is the application of low-temperature gas plasma with low pressure as a source of particles for material treatment. This plasma is a weakly ionized gas (degree of ionization of a percent) consisting of a mixture of stable and excited atoms and molecules, products of the dissociation of molecules: radicals, electrons, positively and negatively charged ions. Modifying of surface properties in these cases is defined by both the radiation damage of the surface structure and physico-chemical interaction with components of the plasma particles of the irradiated material.

As regards the oxide materials, a special interest is the investigations of the effect of ion-plasma treatment in different atmosphere on the efficiency of the proceeding of diffusion-controlled oxidation-reduction processes which largely determine the stoichiometry of the surface layers and coatings, and are the basis of planar manufacturing technology of electronic devices.

Thus, in this work using the lithium-titanium-zinc ferrite ceramics as an example, we examined the effect of nitrogen, oxygen and argon plasma on the proceeding of diffusion-controlled oxidation-



reduction processes having a significant role in the formation of the physical properties of the oxide materials. This investigations subject is preferred because the ferrites are characterized by the high electrical conductivity at high-temperature and, consequently, this greatly facilitates plasma treatment of the ferrites. When using high resistance oxide dielectric materials for these purposes, this procedure is complicated because of the effect of surface charging.

2. Experimental

The experiments were carried out on lithium-titanium-zinc ferrites produced by ceramic technology from a mechanical mixture with the following composition (in wt%): Li_2CO_3 – 11.2; MnO – 2.7; TiO_2 – 18.65; ZnO – 7.6; Fe_2O_3 – 59.81.

The ferrite samples were produced by one-sided pressing in the form of tablets with a diameter of 18 mm, thickness 3 mm. The sintering temperature was 1283 K. Depending on the sintering time, samples were obtained with different stoichiometric composition, which is estimated by the γ value (degree of deviation from stoichiometry) [8-9]. The chemical composition of the sintered ferrites was $\text{Li}_{0.649}\text{Fe}_{1.598}\text{Ti}_{0.5}\text{Zn}_{0.2}\text{Mn}_{0.051}\text{O}_{4-\gamma}$.

In the present work, ion-plasma treatment was carried out using a plasma generator based on a non-self-arc low-pressure discharge in the equipment of the Institute of High Current Electronics SB RAS, which was detailed in [10]. The presence of semiconductor properties in the test ferrite materials allows carrying out its processing on DC.

A vacuum chamber with a volume of 0.5 m^3 was evacuated to a pressure of 1 Pa, and then the ionized gas was supplied into the chamber. A discharge current of 80 A produced in the chamber a uniform gas-discharge plasma with a concentration in the center of the chamber of 10^{10} cm^{-3} and resulted in the density of the saturation ion current up to 10 mA/cm^2 . The nitrogen, oxygen and argon gases were used. The gas was supplied through the cathode section of plasma generator, and consequently, it was possible to control the concentration of reactive gas ions in the chamber. To intensify a treatment process, a negative bias voltage of up to 400 V was supplied to the samples. The thermal heating of the samples was carried out by the stream of ions extracted from the discharge plasma and accelerated in the discharge space layer formed at the surface of the samples when submitting them negative bias. The energy of the accelerated single-charged ions corresponded to the bias voltage. The calculations show that with such energy ions penetrate into the surface layer of the ferrite samples to a depth not exceeding 20–40 Å. In order to ensure the required temperature, ion treatment was combined with electron heating. In this case, electron heating is 2/3 times of plasma treatment. Electron heating was carried out by supplying the anode potential to the samples. The discharge current was 50 A, the discharge voltage was 50 V. The procedure allows to heat the samples to temperatures of 970–1070 K.

The effect of plasma was determined by comparison with the investigation results derived from the samples subjected to heat treatment in non-ionized gas atmosphere at low pressure. The pressure of the gas (P), temperature (T) and annealing down (t) in the gas atmosphere corresponded to the pressure, temperature and time in plasma treatment, and the values for nitrogen were $P_{\text{N}_2} = 10^{-3} \text{ mm Hg}$, $T = 1000 \text{ K}$, $t = 2 \text{ h}$; for oxygen $P_{\text{O}_2} = 4 \times 10^{-3} \text{ mm Hg}$, $T = 1020 \text{ K}$, $t = 1 \text{ h}$; for argon $P_{\text{Ar}} = 6 \times 10^{-3} \text{ mm Hg}$, $T = 1020 \text{ K}$, $t = 1 \text{ h}$. Measuring the thickness of the samples before and after ion-plasma treatment showed the absence of appreciable surface sputtering of samples.

The variation of the oxygen concentration and the nature of the process (oxidation or reduction) in the ferrite samples were evaluated based on the variation of the activation energy of electrical conductivity (E_a) in the depth of the sample. As shown in [11], the value of E_a is correlated with oxygen content in grain boundaries of polycrystalline ferrite, and increases with oxidation of ferrite and, on the other hand, decreases during the reduction process. The activation energy was calculated from electrical conductivity measured in the temperature range 300–550 K by two-probe method after consecutive removing of thin layers from the ferrite sample.

3. Results and discussion

The samples of two types differing in the initial degree of oxidation were investigated. The first type – the A samples were oxygen deficient and had the uniform distribution of oxygen in the sample depth before ion-plasma treatment. The initial oxygen concentration was determined using nuclear microanalysis techniques [12]. The oxygen concentration for these samples was 54.3 at%, and is lower than the value corresponding to stoichiometric composition in the ferrites equal to 57.14 at%. It is estimated that $\gamma = 0.199$ for A samples.

According to the electrical conductivity results, the A samples were a low resistance ($\rho = 10^3$ ohm·cm at $T = 300$ K) with a low value of $E_a = 0.19$ – 0.20 eV in the sample depth (Fig.1a, curves 1). This value of E_a for the polycrystalline ferrite samples corresponds to the minimum difference of oxygen content between grain boundaries and grains.

The second type – the B samples are characterized by 200–300 μm nonuniform distributions of $E_a(x)$ in thin subsurface layers (Fig.1b, curves 1), which were formed during ferrite sintering. The $E_a = 0.75$ eV on the surface, where the grain boundaries are characterized by the maximum oxygen saturation, and changes smoothly up to 0.19–0.2 eV at 250–300 μm depth.

The variation of electrical properties in the course of ferrite heat treatment affects mainly the subsurface layers of the samples. Then the comparative analysis of E_a distribution formed after plasma treatment and thermal annealing was performed.

Figure 1 shows the E_a depth profiles measured before and after thermal annealing in gas and plasma atmospheres for A samples (Fig.1a) and B samples (Fig.1b). It can be seen that the plasma treatment of the ferrite greatly differs from both the annealing in gas atmosphere in the plasma absence at low pressure and the annealing in high vacuum ($P = 10^{-5}$ mm Hg).

3.1. Ion plasma treatment in nitrogen or argon

According to distributions of $E_a(x)$ for both A and B samples, a nitrogen plasma treatment greatly accelerates the process of ferrite reduction, i.e. activates the oxygen diffusion from the samples into the surrounding atmosphere. As a result, the E_a value reduced up to 0.1 eV on sample surface, and then gradually increased to values typical for non-annealed samples at 200–300 μm depth (Fig.1a and Fig.1b, curves 5).

In addition, the sample has been processed in inert gas argon plasma in order to ensure that the observed changes in the activation energy of conductivity are determined by oxygen content variation and not by possible nitrogen diffusion in ferrite.

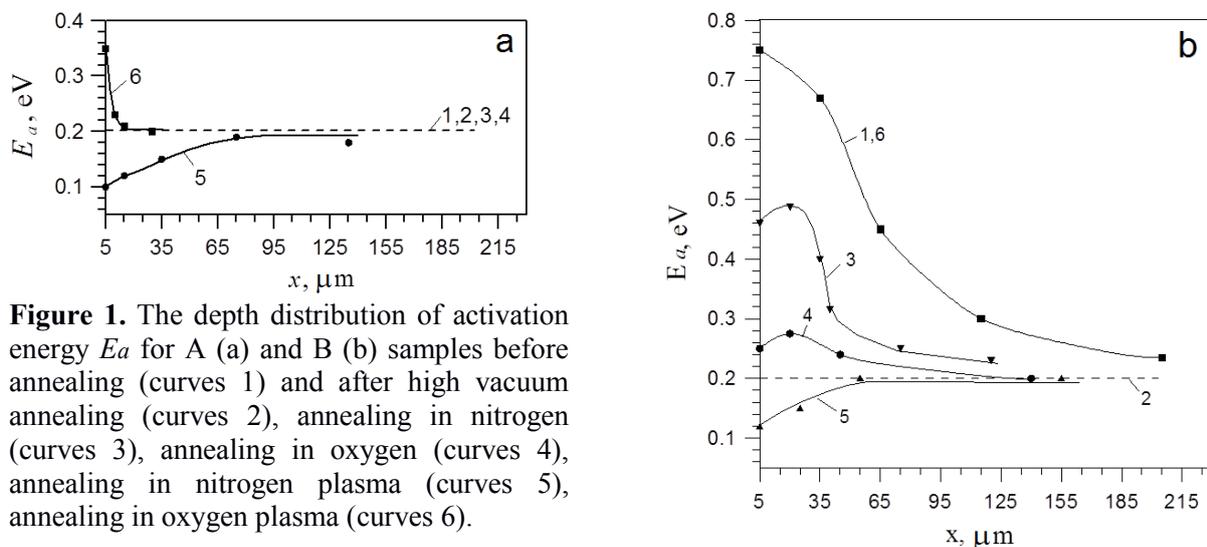


Figure 1. The depth distribution of activation energy E_a for A (a) and B (b) samples before annealing (curves 1) and after high vacuum annealing (curves 2), annealing in nitrogen (curves 3), annealing in oxygen (curves 4), annealing in nitrogen plasma (curves 5), annealing in oxygen plasma (curves 6).

3.2. Ion plasma treatment in oxygen.

According to results, the oxygen plasma treatment of samples affects the direction of the diffusion processes, which in the general case depends on the partial pressure in the surrounding atmosphere. Generally, for samples B, annealing in oxygen (in absence of plasma) results to ferrite reduction due to the loss of the oxygen from the sample (Fig.1b, curves 1, 4). However, oxygen plasma treatment under the same pressure does not change the initial depth profiles of E_a (Fig.1b, curves 1, 6).

This can be explained only by the fact that in the implemented experimental conditions, the oxygen diffusion from the sample surface is balanced by plasma enhanced its direct diffusion into the sample. For non-stoichiometry A samples, annealing in oxygen plasma results to oxidation of the surface layer (Fig.1a, curves 1, 6), regardless of the low oxygen partial pressure, at which the plasma is ignited.

We can explain these results as follows. Effects caused by the ion-plasma treatment may be due to two factors, namely, the state of an ionized gas environment and/or direct effect of their component on the surface layers of ferrite material. The dissociation of the gas molecules occurs in the plasma, causing the formation of reactive components which can strongly interact with the surface of the treated sample. The efficiency of this process increases as a result of the increased energy of the ions, accelerated in the electrical field. In this case, the adsorbed active oxygen at high temperature diffuses into the ferrite predominantly along grain boundaries due to the ceramic structure of ferrite samples. Then oxygen diffuses from the oxidized grain boundaries into the volume of the grains. The potential barrier formed on the boundary depends on the ratio of these diffusion flows, and determines the activation energy of electric conductivity in ferrite.

4. Conclusions

Thus, the ion plasma effect on the oxidation–reduction processes in polycrystalline ferrite has been determined. In particular, the effect is that the high-temperature treatment in polycrystalline ferrites by nitrogen or argon ion plasma greatly accelerates the oxidation-reduction processes in ferrites and changes the process direction depending on the partial pressure of oxygen. Namely, the nitrogen or argon plasma treatment of ferrites speeds up the process of ferrite reduction, i.e. activates an oxygen diffusion from the samples into the surrounding atmosphere. The oxygen plasma effect on the ferrites has a stimulating impact on the diffusion penetration of oxygen into the samples.

In conclusion, the results of this study confirm the active role of accelerated ions of nitrogen in the destruction of the oxide film on the surface of metals and alloys, and as the authors suggested [13], it was one of the reasons for increasing efficiency of nitriding. Previously, nitriding efficiency of these materials is achieved by introducing into the chamber a certain amount of hydrogen.

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