Investigation of the Mechanism of Electronic Conductivity and Parameters of Localized States in Porous Anodic Alumina Films Obtained in Phosphoric Acid

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Abstract—The results of studies of electronic conductivity in annealed films of porous anodic alumina obtained in phosphoric acid are presented. Polarization experiments were carried out for an electrolyte-anodic alumina -aluminum structure in a barrier type electrolyte in the anodic potential sweep mode. It is shown that the initial section of the current curve is described by the theory of a current by a limited space charge for the case of electron traps exponentially distributed over energies in the energy gap of anodic alumina. For porous anodic alumina formed in phosphoric acid, it was experimentally determined that the characteristic energy of the distribution of traps in the band gap of anodic alumina is 0.23 eV.

Keywords—porous anodic alumina; electronic conductivity; phosphoric acid; electron traps

I. INTRODUCTION

Alumina films play an important role in many technologies for the manufacture of electronic products, in particular, such as promising memory elements based on the memristor effect, film capacitors, photo and optoelectronics and gas sensors [1-4]. In recent years, numerous studies have been carried out, and processes for obtaining nanomaterials based on porous anodic alumina are being developed [1,3, 5-7].

Anodic oxide films are an amorphous dielectric material in which the absence of long-range order causes blurring of the edges of the conduction and valence bands. Therefore, the energy bands in such a material cannot be clearly defined as in crystalline materials. The bottom of the conduction band is smeared out, and the tail of the conduction band goes deep into the forbidden zone. The electronic states in the tail of the conduction band are localized and act as traps for electrons. Moreover, the residues of electrolyte anions embedded in the structure of anodic alumina lead to the formation of local defects (electron trapping centers), the parameters and concentration of which are determined by the type of acid used as an anodizing electrolyte.

Alumina is a dielectric material with an extremely low concentration of its own carriers (band gap $E_g \approx 8$ eV). Therefore, the flowing electron current is not associated with its own electrons in the conduction band, but is formed by electrons injected from the cathode. The electrons injected into the dielectric will create a space charge in its volume. The electric field induced by the space charge will be inhomogeneous. Near the anode, it leads to an increase in the total electric field and near the cathode, to a decrease in the field. The flowing electron currents are determined by space charge and are therefore called space charge limited currents (SCLC).

To increase the efficiency of using anodic alumina in various technologies, a deep understanding of the mechanisms of their conductivity and electronic properties is required, which are largely determined by the production modes. The aim of this work was to study the mechanism of conduction in electrolyte-Al_2O_3-Al structures and to determine the parameters of localized states for anodic films obtained in phosphoric acid.

II. EXPERIMENT

Aluminum strips cut from aluminum foil (99.99% purity) were degreased in a hot sodium hydroxide solution, followed by neutralization of the surface in an aqueous solution of nitric acid. Then they were thoroughly washed with distilled water and dried in air. Films of porous anodic alumina were obtained at a constant voltage of 35 V in a 0.4 M aqueous solution of phosphoric acid for 6 minutes (cathode - platinum grid). During the experiments, the temperature of the electrolyte was kept constant at (18 ± 0.5) °C. The voltage was applied to the cell using a P582M potentiostat-galvanostat. After anodizing, the porous alumina films were thoroughly washed with distilled water. Then the obtained samples were annealed in air at 200 °C for 1 h.

To study the mechanism of electronic conductivity in anodic alumina, we used the structure electrolyte - alumina - aluminum. A barrier-type electrolyte was used as one of the electrodes in such a structure. Polarization measurements for annealed films of porous alumina were carried out in an aqueous solution of 0.5 M H_3BO_3 and 0.005 M $Na_2B_4O_7$ in the anode potential scan mode at a rate of 2.6 V / min.

III. THE RESULTS AND DISCUSSION

As shown in [8, 9], freshly anodized films of anodic alumina have filled electron traps in the surface layer of the oxide. Annealing of such anodic films at 200 °C led to the release of electrons from the traps and, as a result, the annealed oxide has empty electron traps in the surface layer [6]. Passing an electric charge through the annealed anodic film leads to filling of electron traps and a change in their electrical resistance. Fig. 1 shows the current curve obtained with polarization in the anodic potential sweep mode at a rate of 2.6 V / min for an annealed film of porous anodic alumina (anodizing electrolyte - phosphoric acid).
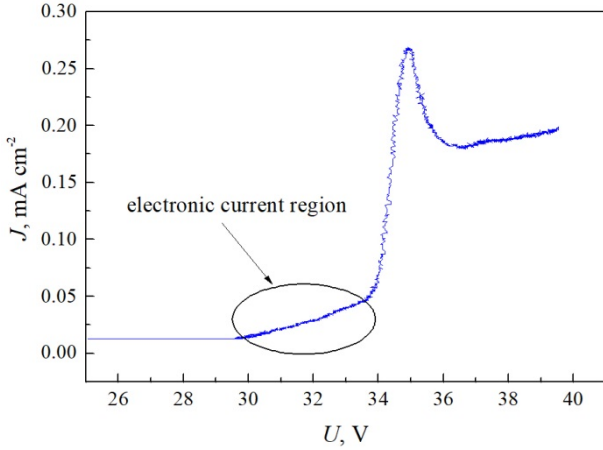

Fig. 1. Current curve obtained with polarization in an electrolyte based on an aqueous solution of 0.5 M H_3BO_3 and 0.005 M $Na_2B_4O_7$ for an annealed film of porous anodic alumina (anodizing electrolyte is an aqueous solution of phosphoric acid, 35 V)

During anodic polarization under the action of a high-intensity electric field and injection of electrons from the electrolyte in anodic alumina, its electronic properties changed - the filling of electron traps formed in the surface layer by embedded residues of electrolyte anions. This process was described by an increase in the current in the initial section of the current curve, which was then followed by a section of an abrupt increase in the ion current (Fig. 2).
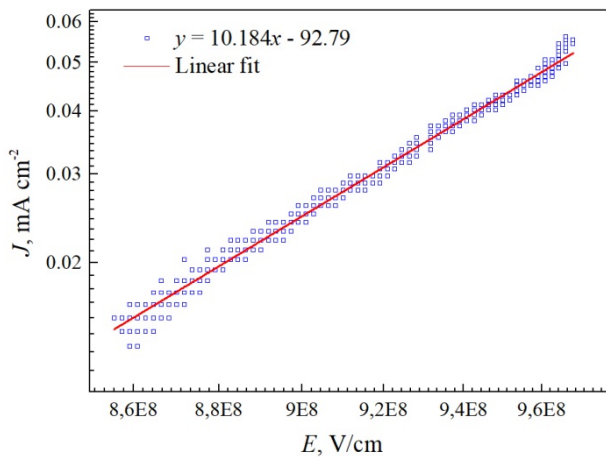

Fig.2. The Current curve in double logarithmic scale for the initial section in Figure 1

An analysis of the current curve at the initial stage of growth made it possible to conclude that the conductivity of the Al_2O_3 anode films is described by the theory of the current by limited space charge for the case of electron traps exponentially distributed in energy.

The exponential distribution of traps in the energy gap of a dielectric is described using the parameter E_t, which is the characteristic energy of the decay of the trap density (Fig.3).
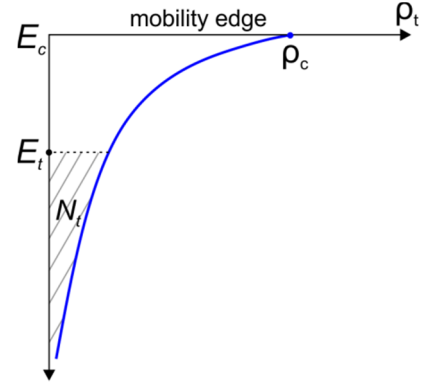

Fig. 3. Energy diagram of an amorphous dielectric for the case of shallow traps exponentially distributed over energies in the band gap. Below the characteristic energy of the distribution of traps E_t, all traps in the tail are filled with electrons. (ρ_t – the density of traps, E_t – the depth of occurrence of traps, N_t – the concentration of filled electron traps)

The larger E_t, the slower the trap density decreases, and the trap tail penetrates deeper into the forbidden zone. The current density in this case is described by the following equation [10].

$$J = N_c \mu e^{1-l} \left(\frac{\varepsilon \varepsilon_0 l}{N_t(l+1)}\right)^l \left(\frac{2l+1}{l+1}\right)^{l+1} \frac{U^{l+1}}{d^{2l+1}}, \quad (1)$$

where N_c is the effective density of quantum states in the conduction band of Al_2O_3;

ε - the relative dielectric constant of Al_2O_3;
ε_0 - vacuum constant;
μ - the mobility of electrons;
N_t - the concentration of electron traps in the Al_2O_3 film;
d - the thickness of the oxide film;
e - the electron charge.

According to the equation (1) the exponent $(l=m-1)$ can be find from a slope of current-voltage characteristics (m) in double logarithmic scale (Fig. 2).

For more informational content a graph showing the variation of current density J vs. the electric field E is plotted. The experimental curve plotted in logarithmic coordinates of the dependence of $\log J$ on $\log E$ – electric field strength (Fig. 2) gives a straight line with a slope $(l + 1)$ equal to 10.184. Knowing the value of l, from (1) one can determine E_t, the characteristic energy of the energy distribution of the traps. The calculations performed give the value $E_t = 0.23$ eV for the characteristic energy of the distribution of traps in the band gap of anodic alumina obtained in phosphoric acid. It can be noted that anodic alumina formed in phosphoric acid has a deeper level of trapping compared to anodic alumina obtained in sulfuric ($E_t = 0.147$ eV) and oxalic acid ($E_t = 0.06$ eV) [11].

The emergence of localized states (electron traps) in anodic alumina is associated with a local disturbance in the ordering of the oxide structure due to the formation of structural defects upon the inclusion of residual electrolyte

anions. As a first approximation, it can be assumed that the larger the atomic size of the main element of the anodizing acid is, the more disordered the structure of the anodic oxide in the places of the defects and the deeper the electron traps will be formed. The atomic radii of the elements P (0.098 nm), S (0.088 nm), C (0.067 nm), as they decrease, are arranged in the following order P > S > C. Consequently, the trap depth should decrease in the same order. This result fully correlates with the depth values traps in anodic alumina formed in phosphoric, sulfuric and oxalic acids.

IV. CONCLUSIONS

The mechanism of conductivity in the structure of electrolyte-Al_2O_3-Al with annealed anodic alumina in the initial section of the current curve is described by the theory of limited space charge current for the case of electron traps distributed exponentially in energy in the forbidden zone.

In the case of films of porous anodic alumina formed in phosphoric acid, localized electronic states are formed in the band gap of anodic alumina, for which the characteristic energy of the trap distribution (E_t) is 0.23 eV.

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