Electro-physical properties of porous anodic alumina films for sensitive elements of MEMS

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Abstract. The results of a comprehensive study of porous alumina film electrical properties obtained by anodizing in acid electrolytes have been presented. The relationship was established between the structure of oxide films, the mechanism of their formation, as well as physicochemical characteristics. A targeted effect on the microstructure of the films made it possible to control their properties by varying the technological parameters without a radical change in the method. This made it possible to predict the behavior of nanostructures and properties for sensitive MEMS elements.

1. Introduction

In recent years, in connection with the development of solid-state devices and integrated circuits, research has been carried out on the mechanisms of charge transfer through thin oxide films, which has made it possible to accumulate a lot of information about their various properties (dielectric constant, breakdown, losses, etc.). However, the available information is far from complete, and in some cases contradicts each other [1, 2]. The discrepancy between the data can be caused by such factors as purity, degree of homogeneity, stoichiometry, conditions for obtaining films, etc. One of the reasons for the relatively slow introduction of anodizing technology into electronics, most likely, is not only the novelty of this method and the absence of industrial-technological installations, as well as any generalizing works considering the properties of films and the possibility of their use, how much in the poor knowledge of the relationship between the mechanisms obtaining and physical properties of films. All this requires studying the properties of oxide films for specific conditions of deposition and application.

When designing MEMS, special attention is paid to the material of the sensitive element, its mechanical and physical-electrical properties [1, 2]. In this work, we studied nanoporous anodic alumina (NAA) obtained by self-ordered anodization (figure 1a) [3, 4].

2. Experimental part

2.1. Determination of dielectric constant and losses in films

The thickness of oxide nanomembranes was measured using optical methods on an MII-4 interferometer. The ellipsometric method made it possible to most accurately measure the thickness of the films (error <10 nm) and their refractive index. For comparative studies, electrical parameters such as breakdown voltage and dielectric strength were measured.
The determination of the membrane dielectric constant was carried out by the capacitor method. The contact was carried out until the maximum capacity was reached: a sample with deposited aluminum electrodes (400 nm thick and 1.0×10^{-5} m² in area) was pressed by vacuum to the table, which simultaneously served as a contact for the measuring circuit; the second contact was a metal rod. With the help of the hold-down contact, we ensured that the capacitance of the contact \( C_c \) was greater than the true capacitance \( C_d \) (\( C_c > C_d \)). Since the \( C_c \) and \( C_d \) are connected in series in the circuit, the measured capacitance was determined as the sum of the true capacitance and the capacitance of the supply wires (the capacity of the supply wires was approximately (6±1) pF and then subtracted from the measured capacitance). The formula was used to determine the dielectric constant:

\[
C = 0.0084 \frac{\varepsilon \cdot S}{d}
\]

where \( S \) is the contact area; \( d \) - film thickness. The measurement was carried out by the zero method on a P577 class I instrument at an operating frequency of 1000 Hz. The data on the dielectric constant and the tangent of the dielectric loss angle are given in the table.

2.2. Measurement of electrical resistance at high temperatures

The information available in the literature [5, 6] on the temperature dependence of the film insulating ability is very limited, which required a detailed study of the dielectric properties of the obtained nanomembranes. Measurement of the true insulation resistance depends on the value of the conduction current caused by ionic impurities and the charge adsorption current, especially since the synthesis of nanomembranes (figure 1a) took place as a result of anodization (electrochemical oxidation) [3–5]. When studying high values of resistance, it became necessary to take into account volume and surface electrical resistance. Therefore, to eliminate the effect of surface conductivity, a screen - "guard" ring was applied to the insulating layer. The electrical circuit for measuring the resistance is shown in Figure 1b. The investigated dielectric film I was placed in a specially made shielded thermostated cell on the lower electrode, made in the form of a table, and pressed by the upper measuring electrode 2 and the electrode - "guard ring" 3, to which one and the same potential, which made it possible to eliminate the influence of surface phenomena. The system of electrodes was heated by stove 9, which is an alundum tube with a nichrome spiral wound around it. The temperature on the sample was controlled by a chromel-alumel thermocouple 10 and a voltammeter 11, type 1108. The voltage was applied to the electrodes from a DC voltage stabilizer 5 of the U1136 type, the signal was amplified by an electrometric amplifier 6 of the U5 - 7 type and was read from a digital voltmeter 7, type B7 - 27 A/1.

![Figure 1](image)
AC bridge P5010 8 was used to measure the dielectric characteristics of the films. Gallet switch 4 was used to serially connect either an AC bridge or an electrometric amplifier to the circuit. To prevent oxidizing electrodes at elevated temperatures, the system of electrodes with a film was placed in an inert gas environment. The method for measuring the electrical resistance of dielectric films using electrodes with a guard ring was the most acceptable for the following reasons. When the potential of the ring and the inner electrode coincided, there was an obstacle to the flow of surface currents between the electrodes. Consequently, the current flowing in the internal electrode circuit passed through the dielectric volume and reached the lower electrode.

2.3. Determination of the frequency dependence of capacitance and dielectric losses
The measurement of dynamic characteristics - the frequency dependence of the capacitance and the dielectric loss tangent - was carried out in the frequency range from 20 Hz to $10^5$ Hz and discretely at a frequency of $10^6$ Hz. KSO-13 capacitor was used as a reference capacitance, where the dielectric material is mica, $C_e = 10^4$ pF, $V$ is a fixed voltage independent of frequency.

3. Results and discussion
Readings of the instrument scale were taken three minutes after the voltage was applied to the electrodes when measuring the films resistance. This time delay made it possible to take into account the current adsorption (Fig. 2). In figure 2a, it can be seen that the electrical resistance of the aluminum oxide films at room temperature had a high value ~$10^{11}$ Ohm. Attention is drawn to the fact that when the film was heated to 160 °C, an increase in resistance was observed to a value of $5.3 \cdot 10^{11}$ Ohm.

![Figure 2. Logarithmic dependence of the electrical resistance of alumina nanomembranes on temperature (a); dependence of alumina films capacity on temperature (b); frequency dependence of capacitance (c); frequency dependence of loss tangent for films formed in anodic alumina films formed in oxalic aqueous solutions (d).](image_url)

This phenomenon is associated with the loss of crystallization water, which leads to the structure densification, and is characteristic of all oxide coatings obtained by electrochemical etching. Further
heating led to a decrease in electrical resistance to \((6 \pm 1) \times 10^7\) Ohm at 500 °C. Thus, although there was a tendency towards a decrease in electrical resistance, the very value of the latter retained high values (not lower than \(10^7\) Ohm), up to a temperature of 500 °C. Frequency dependences of capacitance and dielectric loss tangent at different temperatures for alumina films are shown in Figure 2b. The results showed that the capacity of anodizing aluminum oxide films is almost independent of temperature, and only at frequencies below \(10^3\) Hz, a slight increase in the capacity value with increasing temperature has been observed. By measuring the dependence of the capacitance vs temperature, information was obtained on the linear expansion of dielectric films. From figure 2b the temperature coefficient of the capacity TKC = \(5.4 \times 10^{-5}\) l/deg. was found. Taking into account that for polar dielectrics the dielectric constant decreases with temperature, as well as the Clausius-Mossoti formula, the linear temperature coefficient of the obtained nanomembranes has been calculated: \(\alpha \geq 5.4 \times 10^{-5}\) l/grad. The temperature dependence of dielectric losses had the same character, i.e. the absolute value of dielectric losses increased with increasing temperature (Figure 2c, d). The upward trend was more evident at low frequencies. It should be noted that losses are a bulk property of the dielectric and do not depend on the film thickness. These losses are critical at low frequencies and elevated temperatures.

The study of breakdown and dielectric strength of dielectric films is of practical interest in connection with their use in thin-film capacitors. Electric strength is characterized by the value of the breakdown voltage, in other words, this is the value of the electric field at which breakdown occurs and the dielectric film loses its insulating properties. Breakdown of dielectric films can be caused by both thermal and electrical processes. There are many methods for determining the breakdown voltage of dielectric films, for example, using an automatic measuring device [7–8]. We used the method of non-destructive breakdown voltage determination in MDM structures, which consisted in recording the voltage dependence across the sample on time when passing a fixed current through it. The method made it possible to use a current increased by almost 10 times, and significantly reduce the measurement time of the breakdown voltage when measuring the current-voltage characteristics (CVC). To measure the current-voltage characteristic, the change in current with increasing voltage on the dielectric film, as well as the voltage of the beginning and end of sparking (micro-breakdowns), as well as the voltage of complete loss of insulating properties from the side of the film, were carried out continuously. As a result of the experiments, it was revealed that with increasing voltage at the initial moment, separate flashes appeared, corresponding to breakdowns, the number of which increased with increasing voltage. Then the upper electrode burned out around the puncture sites until the upper electrode burned out in the place opposite to the edge of the lower electrode, after which the breakdown phenomena ceased. The burnout of the electrodes, apparently, occurred as a result of the successive rupture of the dielectric film from the formed edges of the electrodes. The number of breakdowns preceding the burnout of the electrodes decreased with an increase in the thickness of the dielectric film. Thus, one can unambiguously judge only the voltage of the first breakdown (in this work, it is this voltage that was taken as the breakdown voltage).

During the experiments, the following patterns were noted. Most of the discharges occurred over the area of the electrodes, while the percentage of discharges with the positive upper electrode was less than with the negative upper electrode. The dielectric strength in the case of a discharge over the area of the capacitor was significantly higher when the upper electrode had a positive polarity. The noted effect of polarity indicates the existing role of electrons in the process of dielectric breakdown. It can be assumed that the breakdown of thin alumina films is associated with the melting of the dielectric by the electron emission current from the tips, which are always present on the cathode surface. The melting of the dielectric could be accompanied by the release of a conductive component (metal) into the breakdown channel.

Figure 3a shows the dielectric strength dependence on the film thickness, which has a power-law character in the thickness range from 200 nm to 800 nm. With an increase in the film thickness the dependence became weak and practically disappeared at thicknesses over 1000 nm. This work does not provide quantitative relationships between theoretical and experimental data on the breakdown of
alumina nanomembranes, since many of its electrophysical characteristics (impact ionization coefficient, micropore size, potential barrier on contact with aluminum, etc.) are still unknown. Figure 3b shows the dependence of the dielectric strength of aluminum oxide films on temperature (measurements were made at a constant voltage U = 15 V). From the experimental data it follows that the dielectric strength changed little with temperature, and the breakdown unipolarity remained up to 300 °C. It can be assumed that, due to the high mobility of carriers in a dielectric film, as the temperature rises, conditions are created for the resorption of the region of negative space charge and the escape of ions from this region, which leads to a decrease in the dielectric strength with increasing temperature.

Figure 3. Logarithmic dependence of the film dielectric strength on the thickness (a): 1 - the upper electrode with a negative potential; 2 - upper electrode with positive potential. Dependence of dielectric strength on temperature (b): Current-voltage characteristics of films kept at different temperatures (c): 1 - CVC at 22 °C; 2 - CVC at 100 °C; 3 - CVC at 300 °C; 4 - CVC at 400 °C; 5 - CVC at 500 °C.

The current-voltage characteristic (CVC) of the dielectric film was measured at room temperature and direct current. Figure 3c shows the change nature in the current through the sample as a function of temperature. The reproducibility of data from sample to sample ranged from 5 to 10%. From the given CVC, it can be concluded that at room temperature at various voltages (up to 300 V), no significant irreversible phenomena occurred: the insulation resistance remained constant; the number of pores did not change. Holding the samples for two hours at a temperature of 200 °C also did not change the resistance value of the dielectric film of aluminum oxide. Above 300 °C, the resistance of the films decreased.

4. Conclusions
The objects of study were alumina nanomembranes obtained by anodizing aluminum in acidic electrolytes. For the initial and heat-treated samples, the resistance, dielectric loss tangent (tg δ), dielectric constant (ε), and electrical strength have been measured. With an increase in the temperature and time of heat treatment, a significant decrease in the strength properties and an increase in the tan δ of the films were observed; resistance and dielectric constant underwent slight changes.

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