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STRUCTURE AND PROPERTIES OF NANOPOROUS OXIDE DIELECTRICS MODIFIED BY CARBON

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Abstract. A physical method of receiving nanoporous films of the silicon dioxide (SiO_2) and tantalum pentoxide (Ta_2O_5) in vacuum conditions is brought forward in this work. The structure and properties of nanoporous films received as a result of self-organization at magnetron spattering of a compound target are researched in it. Correlations of the quantity and size of pores, the structure and properties of nanoporous films are determined, as well. The self-organization process proves to form spatially spattered pores, to change electrophysical properties of dielectric films and it enlarges their functions.
Keywords: nanoporous oxide films, carbon, self-organization process, magnetron spattering

1. Introduction

The study of nanoporous dielectric films has been set a new impulse of late as a result of substantially enlarged sphere of their practical use. Such films can be used both in microelectronics as insulating stuff with low dielectric permittivity, and they can be used in photonics as anti-reflection coating in optoelectronic devices [1,2]. The nanoporous dielectric films can be also used as basic material for receiving nanomembranes and selective gas-sensing, sensor devices [3,4]. A number of methods of receiving nanoporous dielectric structure were worked out – anodizing, zol-gel method, matrix template synthesis are among them [2,5,6]. All the enumerated methods are chemical which makes it difficult to use them when producing micro – and nanoelectronics devices.

The purpose of the given research is to work out the integral schemes of the formation methods of nanoporous films of the silicon dioxide (SiO_2) and tantalum pentoxide (Ta_2O_5) basing on the technological modes of forming films with their structural and electrophysical properties.

2. Experiment and measurement methods

The basis of the suggested method is the self-organization principle proceeding in the plasma glow discharge which is formed by DC magnetron spattering source, compound spattering targets Si:C (graphite) or Ta:C (graphite) being its cathode [7]. The graphite area on the compound spattering target expressed in percentage - S_c varied in such a case, which resulted in changing the pore quantity and size. Spattering was done in the oxygen atmosphere with the pressure in an evacuated vessel equal to 4×10^{-1} Pa. Such are the conditions under which dielectric films of the silicon dioxide (SiO_2) and tantalum pentoxide (Ta_2O_5) are received, and injecting carbon is to make a sound nanoporous structure. The given method was patented earlier and it was used for receiving the films SiO_2 with low dielectric permittivity [8]. This method, however, is supposed to be applied to other oxide films used in micro – and

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nanoelectronics, in Ta_2O_5 in particular. The pore formation in this process is explained by gaseous compounds CO or CO_2 which on educing, make the film friable forming in it open pores and gas inclusions.

The thickness of the dielectric films which were researched in the electrophysical operations was 100 nm. The films Al, about 100 nm thick, were used as electrodes at electrical measurements. These films were made by means of thermal evaporation in vacuum. Condensing structures Al-SiO_2-Al and Al-Ta_2O_5-Al were formed like matrixes with the active area of 1x1 mm on the ceramized substrates of 60×48×0.6 mm in size.

The determination of the pore quantity and size was done by means of electrochemical copper jumping. The width of the Tauc gap (Et) was defined by the extrapolation $(\alpha E)^{1/2}$ dependence on the photon energy E in the range of the wave lengths of 200-1100 nm [9]. The spectral dependence of the film absorption index (α) was defined by transmission and reflection spectrums with the help of spectrometer USB2000. The determination of the thickness and dielectric film refraction index was stated by means of a spectral ellipsometric complex. The microanalysis was done with the help of the Bruker Quantax 50 EDX microanalyzer as a part of an electron microscope Hitachi TM-1000. The spectral analysis of the researched films was done by using an IR –spectrometer in the range of the frequencies of 500 – 5000 sm^{-1}.

3. Experiment results and analysis

Electric properties. The research of the electric capacity of the structures Al-SiO_2-Al and Al-Ta_2O_5-Al has revealed the general tendency of dielectric permittivity changing and that of angle tangent of dielectric losses with the increase percentage of graphite content on the compound target when S_c < 40%, however, at great values of S_c the qualitative type of dependences differed. At the same time the dependence of electric strength on S_c was similar, and it decreased gradually for the both structures (Fig. 1, Fig. 2)

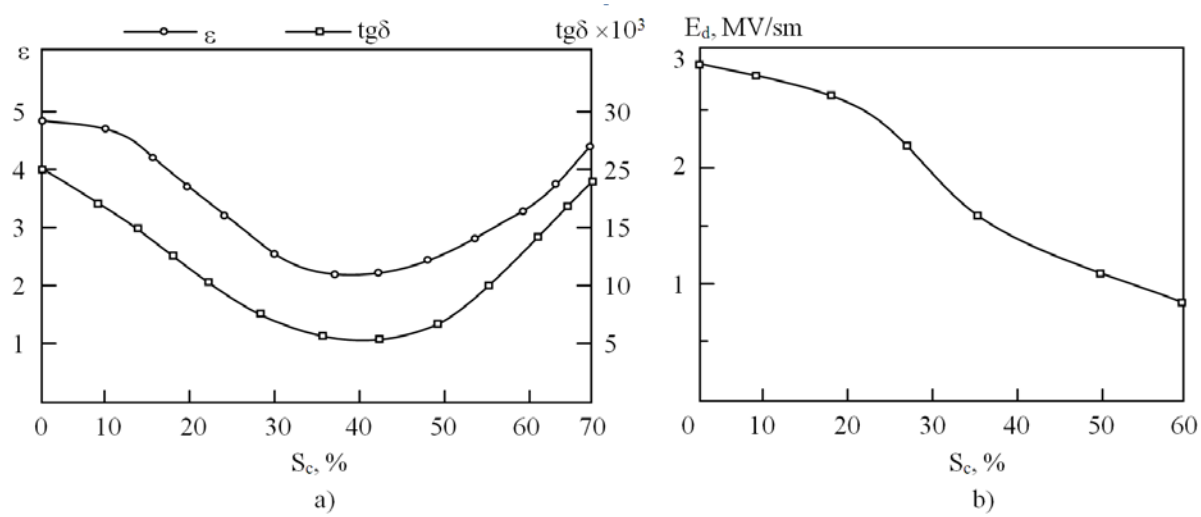

Fig. 1. Dependence of dielectric permittivity ε, tangent losses tgδ (a) and electric strength Ed on S_c (b) for the structure Al-SiO_2-Al

It is evident that the reduction of dielectric permittivity for films SiO_2 can be explained only by the formation of gas inclusions, because all the other possible ways (the formation of chemical bonds of silicon with carbon, the formation of carbon injections) would lead to an opposite result. The tangent reduction of the dielectric loss angle is supposedly connected both with the gas inclusions, having a considerably smaller tangent of loss angle, and also with the reduced film defect because of the chemical reactions which are supposed to be more

intensive in the places of defect localization. The growth of these values at $S_c > 40\%$ is caused by the oxygen deficit and formation of films SiO_x, in which x proceeds to 1 which can result in the formation of local regions containing underoxidized silicon and, hence, can enlarge tangent of dielectric loss angle. This is verified by the microanalysis, Auger electron spectroscopy (AES) and IR-spectroscopy data. Electric strength reduction is quite characteristic of nanoporous films that have heterogeneous structure, and probably, it is connected with penetration of the material of the upper electrode into the dielectric film [10].

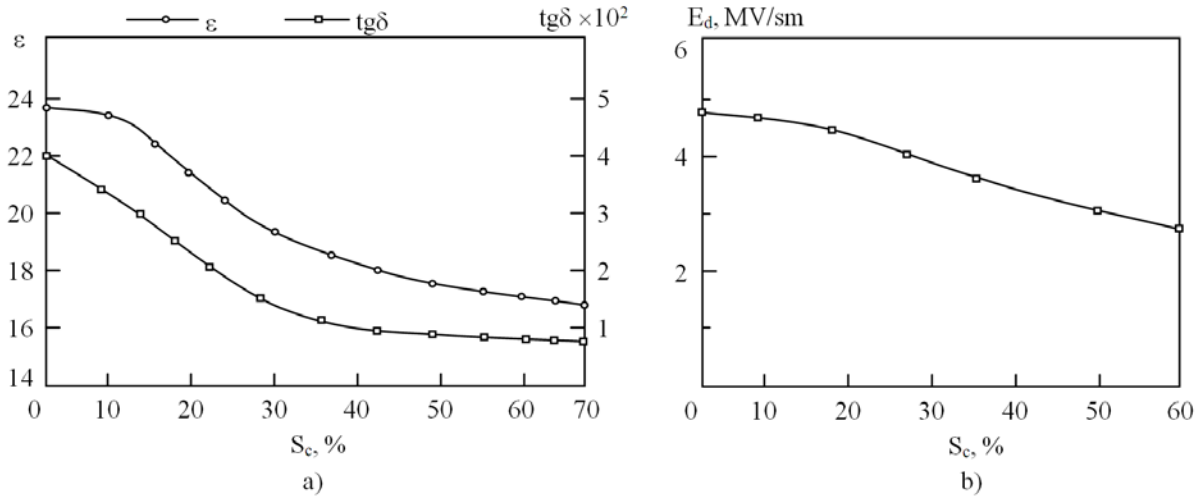

Fig. 2. Dependence of dielectric permittivity ε, tangent losses tgδ (a) and electric strength Ed on S_c (b) for the structure Al-Ta_2O_5-Al

On the analogy of the previous account, the same changes are supposed to occur in the films Ta_2O_5, however, the dependence type in them is somewhat different, which can be explained by the chemical properties of Ta, itself.

Optical properties. The research of physical properties of dielectric films SiO_2 and Ta_2O_5 has revealed the change of the refraction index n and the width of the optical gap Et (Fig. 3).

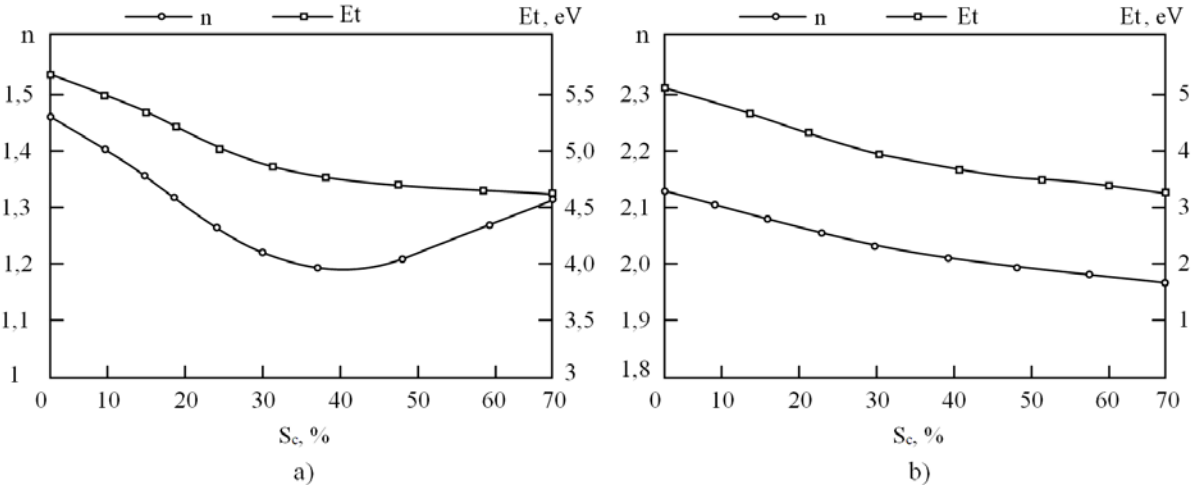

Fig. 3. Refraction index dependence n (at the wavelength λ=632 nm) and that of the width of the optical gap Et on S_c for the structure Al-SiO_2-Al (a) and Al-Ta_2O_5-Al (b)

The behaviour of the refraction index correlates with the change of dielectric permittivity, which is quite conformable to the theory. Reduction of the width of the optical

gap can be connected both with the electronic structure change of dielectric films, themselves, and the presence of gas in the pores.

Structure of surface. The research of the dielectric film porosity illustrated quite even distribution of the pores over the dielectric area. Small mesopores with the diameter of less than 10 nm and larger ones with the diameter of more than 50 nm can be visually distinguished [11]. The porosity of the film SiO_2 considerably rises with the value growth of S_c reaching its peak at S_c ~50%, then the growth is replaced by the saturation area (Fig. 4). The qualitative dependence type for the films SiO_2 and Ta_2O_5 is equal, at that. Porosity was determined by capacitance method [12]. The structure of the surface also undergoes considerable changes (Fig. 5).

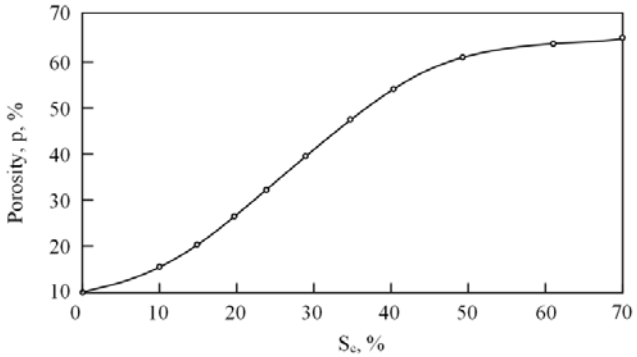

Fig. 4. Relationship between porosity of dielectric film SiO_2 and S_c

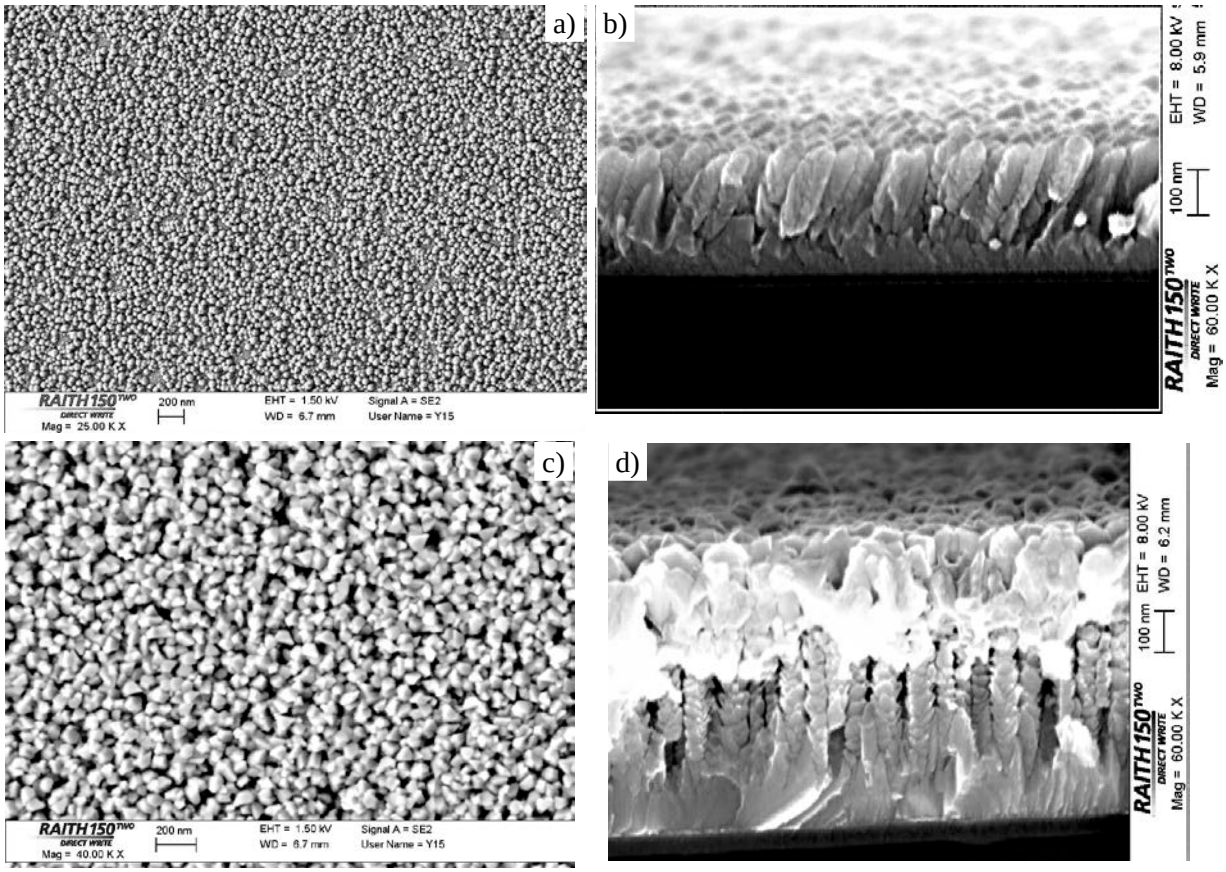

Fig. 5. The surface of the nanoporous dielectric SiO_2 (S_c = 60%) received with the help of the probe microscope: a – surface of the plate, b – chip in the edge of the plate, c – surface of the plate (with an upper aluminium electrode with a thickness of 200 nm) d – chip in the edge of the plate (with an upper aluminium electrode with a thickness of 200 nm)

Spectral analysis. The analysis of the structure of the researched films SiO_2 done by a microanalyzer revealed some rise of oxygen content with the growth of Sc, the same concerned the films Ta_2O_5. Moreover, IR spectrums of the researched films proved a sharp growth of absorption at the wavelength ν=2350 sm^{-1} corresponding to oscillations of bonds C–O. There are also changes in the area: ν_1 =3000 sm^{-1}, ν_2 =3400 sm^{-1}, ν_3 =3600 sm^{-1}, and also some changes of peak ν_4 =935-940 sm^{-1}. Peaks ν_1, ν_2, ν_3 are usually referred to as OH – groups and H_2O molecules, peak ν_4 refers to Si-O-Si bond (valency oscillations) [13].

Supposedly, it can be explained by the presence of water in the pores owing to the capillary effect, and also to the reaction products – gases CO or CO_2. It can occur, as well, owing to the adsorption of gases CO or CO_2 from the atmosphere [14]. The given peak amplitude rises with the growth of Sc, which can be connected with the occurrence of oxygen vacancies in the silicon and negative charge. The occurrence of the effective negative charge on the silicon atom adds to a better adsorption capacity. Thus this resulted in the stimulated adsorption. The preliminary experiments have already proved the selectivity of hydrocarbons and gas CO adsorption, and also of organic compounds with different functional groups.

4. Conclusions

1. The experiments proved that the carbon injection into the process of the formation of the films SiO_2 and Ta_2O_5 leads to the formation of self-organized nanoporous structure. The size and density of the pores is determined by the quantity of the injected carbon.

2. Electrical and optical parameters of the films SiO_2 and Ta_2O_5 are largely defined by the porosity and they have similar tendencies in some intervals, however, the general dependence type is stated by the chemical properties of the spattered material, itself.

3. Common tendencies in the change of electrophysical properties and in the surface structure of the films SiO_2 and Ta_2O_5 with the carbon injected into them, make it possible to assume that analogous changes will be developed in other oxide dielectrics which are formed in the plasma of the glow discharge, though the qualitative dependence type will be different.

4. The formation of the nanoporous structure contributes to the rise of the selective adsorption capacity of the researched dielectrics, mainly, owing to capillary condensation in mesapores and also stimulated adsorption, which can serve the basis of creating gas-sensing sensor devices [15].

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