CHAPTER «PHYSICAL AND MATHEMATICAL SCIENCES»

CHARGE SELF-ORGANIZATION IN SI – SIO$_2$ STRUCTURES

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Abstract. The *purpose* of the work is to study the mechanisms of charge self-organization in Si – SiO$_2$ structures. *Methodology.* The effects of charge self-organization were studied by the method of thermally stimulated depolarization (TSD) of the original and X-irradiated structures. *Result.* The regularities of the experimental spectra of thermally stimulated depolarization of the original and X-irradiated Si – SiO$_2$ structures were studied. The experimental curves *j(T)* show two characteristic maxima: in the region 360K (low temperature-*LT*) and 450 K (high temperature-*HT*- maximum). Calculation methods based on the solutions of the Fredholm integral equation of the first kind, which describes the experimental spectra of TSD, the energy spectrum of the density of defect states that form the electret state in the region of characteristic maxima *j(T)* is calculated. Activation energies and frequency factors of the corresponding defects are estimated. Interpretation of the results was performed using the model of classical ion traps at the interfacial boundary Si – SiO$_2$ and taking into account the mechanisms of bulk transport of ions (H^+, Na^+) in the structural network of SiO$_2$. Conclusions are made about the nature of polarization of Si – SiO$_2$ structures in the region of *LT*- and *HT*-maxima. *Practical implication.* The obtained results are interpreted from the standpoint of self-organizing processes in the electronic subsystem Si – SiO$_2$, which is considered an open thermodynamic system.It is believed that the transition to the thermodynamic equilibrium state corresponds to the minimum value of the electronic component of the total entropy of the system. The results of

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the work can be a fundamental basis for purposeful control of the electronic properties of heterogeneous structures of micro- and nanoelectronics. *Value/originality.* The results are given on the mechanisms of charge self-organization in Si – SiO_2 structures can be used to create unique structures of electronics, as well as the latest radiation-resistant elements that function in conditions of high fields and powerful radiation effects.

1. Introduction

Structures based on silicon Si – SiO_2 are widely used today as basic elements of modern micro- and nanoelectronics. They are characterized by the presence of interfacial boundaries, which are characterized by mechanical stresses, localized charges, linear defects, impurities, etc. All this generally has a negative impact on the performance of such structures and their stability.

Features of the studied structures are: 1) the interphase boundary formed between two materials of dielectric nature, so the electrical component of the interphase energy will be mainly electrical (dipole) nature; 2) the electric charge, in contrast to Si – Me structures, is spatially distributed in the thickness of the formed layer according to a complex law with its simultaneous localization of high density in the SiO_2 layer directly near the interfacial boundary; 3) interphase interaction in the Si – SiO_2 structure is realized between two materials of different structural ordering (crystal – amorphous medium).

Therefore, it is to be expected that external factors will have a significant effect on the energy spectrum of defects of such a thermodynamically nonequilibrium system. For example, it was found that radiation exposure changes the charge state of defects in the volume of SiO_2 and at the interfacial boundary Si – SiO_2 [1, p. 603; 2, p. 1105; 3, p. 77; 4, p. 151, 235; 5, p. 1841]. This is practically important for the creation of radiation-resistant micro- and nanostructures of electronics and systematic control of their parameters under the action of radiation [1, p. 608]. The fact of localization of mobile Na^+ ions in the SiO_2 layer near the Si surface, which take part in the volume-charge polarization of the gate dielectric of field devices, predicts the creation of new radiation-resistant elion devices [4, p. 221–231]. Under optimal conditions of external influences, the transition of the Si – SiO_2 structure to the equilibrium state can be realized.

From the standpoint of non-equilibrium thermodynamics, such an open system evolves to an equilibrium state not according to the Boltzmann law with increasing entropy, but gradually, with decreasing entropy and the formation of structures of a new type, which are characteristic of quasi-stationary states.

For the studied heterogeneous system, where the processes in the electronic subsystem are decisive, this means the formation of structures with an effective redistribution of charges, which corresponds to the minimum value of the entropy of the electronic component of the system. Moreover, during the transition to a thermodynamically balanced state, charge arrangement has as its goal not only the achievement of neutrality of the structure, but mainly the realization of a thermodynamically balanced state with minimal entropy.

Specific mechanisms of charge self-organization in such heterogeneous structures depend on the structure of the object (presence of interphase boundaries, macrodefects, etc.), as well as on the energy spectrum of defects acting as traps for charge carriers. Therefore, the study of charge effects under the action of external factors allows studying the mechanisms of charge self-organization, which is important for the creation of thermodynamically stable structures of a new type for the needs of micro- and nanoelectronics.

These problems can be solved only with specific information about the structure and energy spectrum of defects induced by radiation. An informative tool in this regard is the method of **t**hermally **s**timulated depolarization (TSD), which has proven to be an effective way [6, p. 45, 97; 7, p. 111–120; 8, p. 93; 9, p. 391], as well as the behavior of mobile ions. However, studies of Si – SiO_2 structures by this technique are currently limited. This is partly due to the ambiguity of the interpretation of experimental spectra, as a number of complex defects take part in repolarization processes: from two-dimensional to zero-dimensional with different electrical activity, and a complex experimental technique.

The *purpose* of this work is to establish the mechanisms of charge self-organization in the original and *X*-irradiated structures Si – SiO_2 structures, using the experimental regularities of the spectra of thermostimulated depolarization and the energy spectrum of defects calculated on their basis.

2. Methods of thermally stimulated depolarization studies

The essence of the technique is the preliminary polarization of the sample at a certain temperature by an external electric field and its subsequent cooling to a lower temperature (eg liquid nitrogen temperature), resulting in a polarized state "freezes", i.e. the relaxation time of this state increases sharply. Turning off the electric field in this state and shorting the electrodes does not lead to noticeable depolarization of the object, because the nonequilibrium state is metastable. When a "frozen" polarized object is heated in a short state, the phenomenon of thermally stimulated depolarization is realized according to a certain time law, which results in a depolarization current flowing in the circuit, which is physically a bias current.

In the first stages of using the TSD technique, researchers limited themselves to stating the presence or absence of certain non-monotonicities in the TSD spectra, and the conclusions were only qualitative and descriptive. The situation has changed significantly since the use of computer tools for processing results and special software resources. This allowed not only to automate the measurement process, but also significantly increased the informativeness of the obtained experimental TSD curves. The use of analytical expressions for thermally stimulated conduction currents, polarization, discharge and depolarization allows to establish a relationship between the parameters of electrically active defects and the position, magnitude and shape of the corresponding peak of thermally stimulated current.

According to the phenomenological theory of current TSD, in disordered dielectrics with a quasi-continuous energy spectrum of electrically active defects, the thermally stimulated current *j(T)* can be described by the Fredholm integral equation of the first kind [6, p. 112; 7, p. 233; 8, p. 167–180; 9, p. 391]:

$$j(T) \sim \int_0^{\omega_e} d\omega \int_0^{E_m} g(E,\omega)\chi(E,\omega,T,\beta)dE, \qquad (1)$$

ω, E –frequency factor and activation energy of electroactive defects, respectively; T – temperature of the object; β is the heating rate of the sample; $g(E,\omega)$ – function of distribution of electroactive defects; $\chi(E,\omega,T,\beta)$ – subintegral function, the specific form of which is determined by the physical model embedded in the theory of TSD.

In the case when the object implements the kinetics of relaxation of the first order (the rate of change of the concentration of charge carriers or polarization of the sample is proportional to the first degree of carrier concentration or polarization, respectively), the function $\chi(E,\omega,T,\beta)$ is:

$$\chi = \frac{\omega}{\beta}\exp\left[-\frac{E}{kT}-\int_{T_0}^{T}\frac{\omega}{\beta}\exp\left(-\frac{E}{kT}\right)dT\right], \tag{2}$$

and equation (1) is transformed into the form:

$$j(T) = \frac{\omega}{\beta}\int_{0}^{E_m} g(E)\exp\left[-\frac{E}{kT}-\int_{T_0}^{T}\frac{\omega_e}{\beta}\exp\left(-\frac{E}{kT}\right)dT\right]dE, \tag{3}$$

where ω_e – is the effective frequency factor.

The energy spectrum of defects is quantified by the function of the density of states *g (E, ω)* obtained from the experimental curves of TSD currents by solving the integral Fredholm equation of the 1-st kind, which describes this process. A mathematical feature of this problem, which is described by Fredholm's equation of the first kind (3), is its Adamard incorrectness (manifested in the fact that small deviations of the measured function *j (T)* may correspond to large deviations of functions *g (E, w*) or *g* (*E*), as well as the fact that for any dependence *j (T)* the solution may not exist at all).

Therefore, the Tikhonov method [10, p. 234], developed for problems of this class and called the regularization method, was used to solve this problem. This method is based on the idea of selecting possible solutions and the concept of regularizing regulator. In practice, the solution is sought by numerical methods, approximating the original infinite problem by some finite dimension.

An important parameter that characterizes electrically active defects or the process of non-isothermal charge relaxation is the frequency factor ω_e. According to the TSD curve, the frequency factor is determined by the formula [6, p. 111]:

$$\omega_e = \frac{W^2\beta}{2k^2T_m^3}\exp\left(\frac{W}{kT_m}\right).$$

We developed an experimental computerized measuring complex and a method for processing the elementary peak of the thermally stimulated current of experimental dependences *j (T)* to determine the activation energy and frequency factor of the center responsible for the observed maximum, described in detail in [11, p. 40].

The described approach is to some extent idealized. In the general case, the distribution of relaxation times may be due to the simultaneous independent distribution of electroactive defects, both in terms of activation energy and frequency factor.That is, it is necessary to consider an object with two-dimensional quasi-continuous distribution of electroactive defects, which is characterized by a two-dimensional distribution function $g(E,\omega)$.

The real spectra of TSD of semiconductor structures, as a rule, have complex functional dependencies, which is graphically represented by the presence of a number of extremes. The latter are known to reflect the processes of excitation and capture of carriers on energy traps located in a certain energy range. Therefore, using mathematical processing of curves, it is possible to obtain quantitative information about the parameters of the centers responsible for the observed phenomena.

3. X – induced defect formation in Si – SiO_2 structures

The (p-Si) -SiO_2 structures formed by industrial technology by combined oxidation of p – Si plates in dry and wet oxygen at a temperature of 1150 °C were studied. The thickness of the SiO_2 layer was 0.26 μm. Infrared spectroscopy was used to identify the defect-impurity structure, in particular, the transmission spectra of the obtained Si – SiO_2 structures at room temperature in the range of 1000-4500 cm^{-1} were studied. In particular, the composition of the film is characterized by the position of the absorption band, located about 1080 cm^{-1} (main band) and 800 cm^{-1}, which are associated with valence and oscillations of the ring structure SiO_4 – tetrahedron in amorphous SiO_2. Absorption bands at 3600 cm^{-1} show the presence of adsorbed and chemically bound water in the layers. The absorption band at 3600 cm^{-1} is due to the presence of silane groups with hydrogen bond on the surface and volume of the layer. The presence of hydrated groups of Si – H type is confirmed by the presence of an *IR*-absorption band of about 2360 cm^{-1}.

Samples for measurements with an area of 1 cm^2 were obtained by scraping the oxidized plate. Polarization of the structures was performed in an electric field between two flat electrodes of a capacitor cell placed in a vacuum cryostat at temperatures of ~ 360 and ~ 450 K, respectively. The magnitude of the polarization field was $2 \cdot 10^4$ V/cm.

The "fixation" of the electret state was carried out by abruptly cooling the polarized structure to room temperature by blowing liquid nitrogen vapor through the channels of the cell heater. After cooling, the structure was heated in a linear mode of temperature change at a rate of 0,06±0,1 К/s with synchronous recording of the depolarization current. The temperature range during the deployment of the spectrum *j (T)* was 293–450 K. The RUP-120 device with a W-tube (I = 2 mA, U = 100 kV) was used as a source of *X*-radiation.

Figure 1 presents typical TSD spectra in the temperature range 293–450 K of the original and irradiated Si – SiO_2 structures obtained by the method described above.

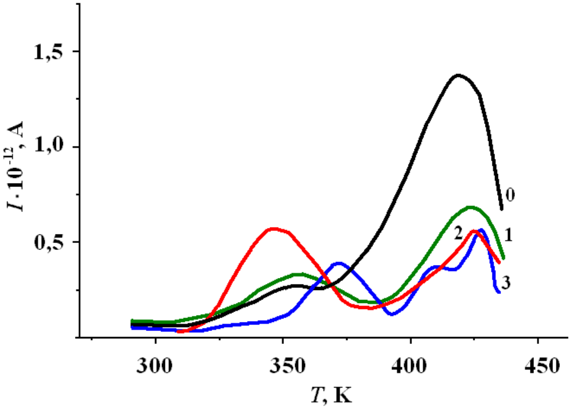


Figure 1. Spectra of currents of thermally stimulated depolarization of the original (0) structure Si – SiO_2 and irradiated with X-quanta at different time exposures: 1 – 20 minutes 2 – 40; 3 – 120

As can be seen, the spectra of the studied structures have two characteristic maxima: low-temperature (*LT*) in the region of ~ 360K and high-temperature (*HT*) ~ 450K. The action of *X*-radiation does not change the general appearance of the experimental dependences *j (T),* but reduces the electret charge accumulated during polarization. A characteristic feature is the increase in the value of the *LT*-maximum with the time of irradiation and the synchronous decrease of the *HT*-maximum with its simultaneous shift to the region of higher temperatures. The *HT*-maximum undergoes certain transformations after large doses of irradiation of structures with a simultaneous shift relative to the position of this extremum in the original sample.

Thus, according to the above results, the depolarization current of the studied Si – SiO_2 structures in the temperature range 293–480 K is formed by two types of carriers: low-energy, released by thermal excitation from low-energy traps (*LT*-maximum, $E_1 \pm \Delta$) and conditionally high-energy released from high-energy traps (*HT*-maximum, $E_2 \pm \Delta$). From the given TSD spectra it is seen that the increase in the irradiation time is accompanied not only by a significant change in the magnitude of the characteristic maxima, but also by the transformation of their structure. The structural rearrangement of the centers under the action of *X*-rays responsible for the maxima in the TSD spectra can be quantified to some extent by the Gaussian peak decomposition method. It is obvious that the "blurring" of the maximum will be accompanied by a complication of the structure of the centers, which will correspond to an increase in the number of relevant "gauss". Figure 2 shows the generalized changes in the number of characteristic Gaussians with the absorbed radiation dose for the *LT*- and *HT*-maxima of the TSD spectrum.

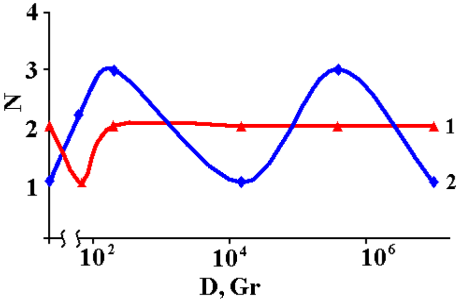
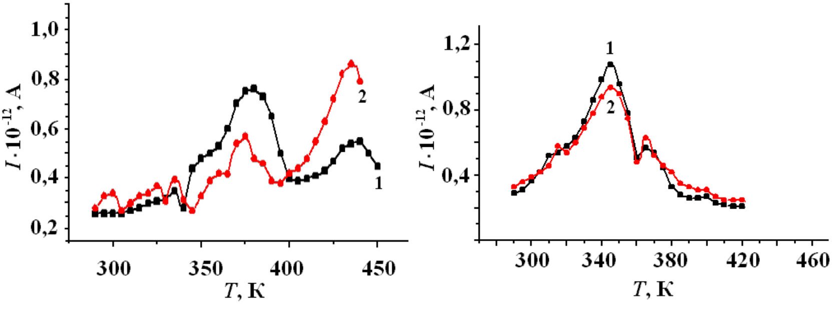


Figure 2. Change in the number of characteristic Gaussians for HT- (1) and LT- (2) maxima with a dose of X-irradiation

As can be seen, the structure of the centers responsible for the *HT*-maximum undergoes structural ordering at a low radiation dose (10^2 Gy), reducing the number of "gauss" to n = 1 and then increases to the initial (n = 2), without changing over time irradiation. The structure of the *LT*- maximum undergoes drastic changes in the studied time interval of irradiations, varying from n = 1 to n = 3, ordering only at certain irradiation times.

Thus, the above results indicate that the main radiation-induced changes in the structure of $Si – SiO_2$ occur due to the processes that form the *LT*-maximum in the spectrum of TSD currents. In order to establish the relationship between the carriers responsible for the formation of the electret charge in the region of *LT*- and *HT*- maxima of experimental *j (T)*, experiments on repolarization of $Si – SiO_2$ structures in the region of characteristic temperature maxima: ~360 and ~450K. The studied structures were previously irradiated with *X*-radiation at T = 293 K, and then 2-3 cycles of "polarization – depolarization" were performed.

In figure 3a, the full spectra of *j(T)* TSD of the $Si – SiO_2$ structure, previously subjected to "polarization – depolarization" cycles (2, 3 cycles) in the region of *HT*-maximum (T = 450 K) are given.



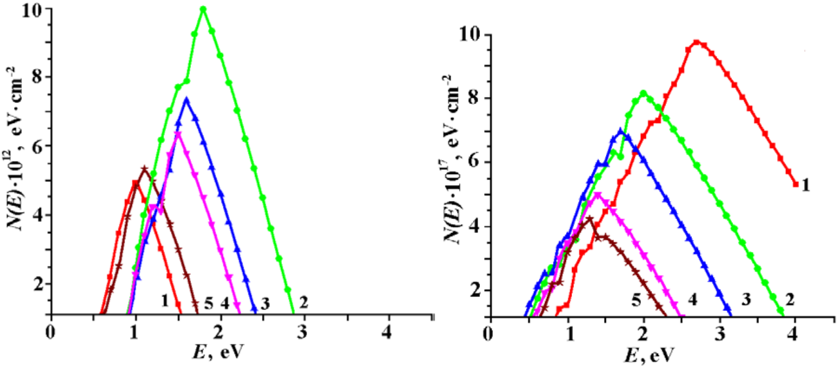
a *b*

Figure 3. Spectra of TSD currents of $Si – SiO_2$ structure after two (1) and three (2) cycles "polarization – depolarization" at different polarization temperatures: *a* – T = 450 K; *b* – 360 K (pre- *X*-irradiation time – 20 min)

As can be seen from the figure, the obtained spectrum of TSD undergoes significant changes compared to the original. In particular, the value of the – maximum increases significantly with the simultaneous complete disappearance in the studied temperature range of the *HT*-maximum. In addition, the position of the *LT*-maximum is shifted to the region of lower temperatures by $\Delta T = 20$ K relative to the similar maximum of the original structure. The described regularities are also performed for other structures of this type with a dose of previous *X*-irradiation up to 106 Gr.

The spectra of *j (T)* structures prepolarized in the region of the *LT*-maximum are significantly different (Figure 3,b). In particular, after double repolarization, the *LT*-maximum increases with a simultaneous decrease in the value of the *HT*-extremum. The performed three cycles "polarization – depolarization" lead to a radically different result, namely to a significant decrease in the *LT* maximum and an increase in the *HT*-maximum on the experimental dependences *j (T).* However, the *HT*-maximum does not disappear. It should be noted that the described changes in the TSD spectra were not detected during the repolarization of Si – SiO_2 structures in the region of room temperatures, as well as without prior radiation treatment. In addition, increasing the number of "polarization – repolarization" stages for more than three cycles does not change the overall appearance of the spectrum *j (T)* in the studied temperature range.

These results indicate the mobile nature of carriers capable of migrating in an amorphous SiO_2 network and filling (releasing) low- and high-energy traps. Taking into account the role of the Si – SiO_2 interfacial boundary in polarization processes leads to the conclusion that it is possible to "electrically" rearrange its relief in "polarization-depolarization" cycles by transforming the structure of hydrogen-containing and defect-impurity complexes and the charge of positive localized ions in the SiO_2 layer near the Si – SiO_2 boundary [4, p. 198; 12, p. 1105; 13, p. 985]. To systematically management the parameters of Si – SiO_2 – based device structures, it is necessary to know the nature of traps for current carriers and their parameters. Some quantitative values, in particular the density of states and their energy distribution can be obtained from the analysis of experimental spectra of TSD currents [6, p. 189]. In practice, the solution is sought by numerical methods, approximating the original infinite problem by some finite dimension. The energy density spectra of the states corresponding to the experimental maxima *j (T)* TSD of the studied Si – SiO_2 structures calculated by this method are shown in Figures 4 a,b.



a *b*

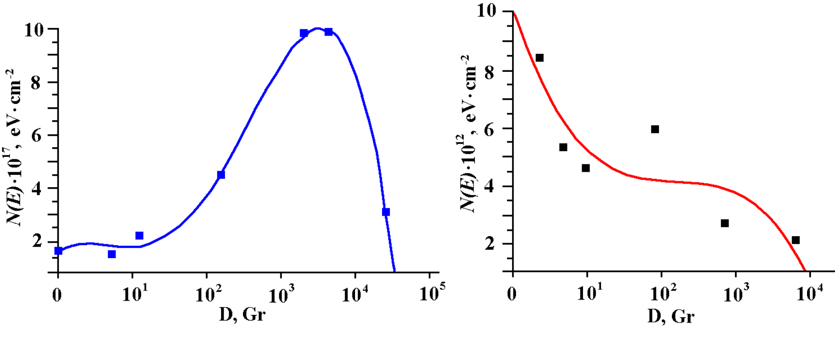
Figure 4. Energy spectrum of density of states in the structure of Si – SiO_2 *X*-irradiation: a – (*LT*-maximum): 1 – activation energy *E* = 0.52 eV; frequency factor *ω* = 2,37 Hz ; 2 – *E* = 1.19 eV, *ω* = 13,1·10^3 Hz; 3 – *E* = 0.63 eV, *ω* = 7 Hz; 4 – *E* = 0.34 eV, *ω* = 0,1 Hz; *ω* = 5 – *E* = 1.02 eV, *ω* = 4,1·10^3 Hz; 6 – *E* = 2.06 eV, *ω* = 5,6·10^8 Hz; *ω* = 7 – *E* = 1.30 eV, *ω* = 53,1·10^3 Hz;

b – (HT-maximum): 1 – activation energy *E* = 1.29 eV; frequency factor *ω* = 7.5 kHz; 2 – *E* = 1.22 eV, *ω* = 3.3 kHz; 3 – *E* = 1.02 eV, *ω* = 250 Hz; 4 – *E* = 0.98 eV, *ω* = 170 Hz; 5 – *E* = 0,73 eV, *ω* = 6.85 Hz; 6 – *E* = 0.88 eV, *ω* = 32.03 Hz

As can be seen, the action of *X*-irradiation changes the maximum value of the density of states N_{max} in the region of both maxima, and also carries out their energy redistribution. The effect of irradiation is accompanied by a significant change in the frequency factors of the centers (traps) responsible for the observed changes, which indicates their significant structural changes.

The kinetics of N_{max} in the irradiation process for both types of maxima *j (T)* is shown in Figure 5 a, b.

As we can see, radiation treatment leads to significantly different behavior of N_{max} with the time of irradiation, which is explained by the different nature of radiation-induced processes in *LT*- and *HT*-traps. In particular, in the region of *LT*-maximum N_{max} almost does not change in



a *b*

Figure 5. Dependence of the maximum value of the density of states on the time of *X*-irradiation: *a* – low temperature maximum (360K); *b* – high temperature maximum (450 K). The points on the graphs are experimental values, and the lines are approximate dependencies

the first stage of irradiation, and then gradually increases to the maximum value (second stage). In general, irradiation is accompanied by a decrease in N_{max} up to values corresponding to the original structure. This fact indicates the structural healing of induced radiation defects and their neutralization.

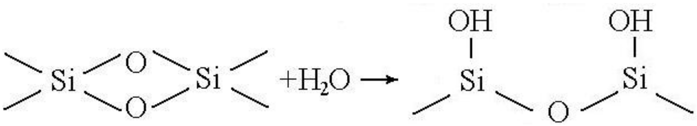
The three-stage dependence of N_{max} on the absorbed radiation dose is also observed for the *HT*-maximum *j (T)* (Figure 5, b). However, the nature of this dependence is significantly different from that described for the *LT*- maximum. In particular, a monotonic decrease in N_{max} is observed throughout the dose range. Moreover, in the first stage (~ 100 min) there is a sharp decrease in N_{max}. The second stage is characterized by the invariance of N_{max} with the absorbed radiation dose. The third stage is characterized by a further monotonic decrease in N_{max}.The obtained dependences testify to the "accumulative" nature of *X*-induced changes due to complex mechanisms of defect transformation and the action of mutually exclusive factors. These are, in particular, the generation and annealing of *X*-induced defects, their healing and reconstruction to thermodynamically equilibrium, neutralization of electrically active defects at the Si – SiO_2 boundary by carriers of the opposite sign with the formation of neutral associates.

4. Nature of charge carriers and mechanisms of their migration in self-organization processes

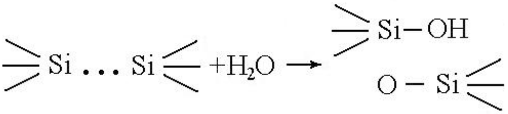
When discussing the nature of thermoactivation processes in the literature, attention is focused mainly on two factors: the participation of hydrogen and alkali metal ions (Na^+, K^+). Experimental data [4, p. 115; 12, p. 1106; 14, p. 680] indicate the multifaceted participation of hydrogen in the formation of the properties of Si and SiO_2. However, if for monocrystalline Si the situation is considered sufficiently understandable [15, p. 231] then the participation of hydrogen in the phenomena of transfer in SiO_2, as well as in the formation of electronic states of the Si – SiO_2 boundary is far from understanding.

A large number and their differences in "hydrogen" models reflects not so much scientific views (models), but primarily the diversity of possible entry of H into the amorphous SiO_2 network and the influence of technological factors – and, consequently, the problem of managing SiO_2 properties [5, p. 1840; 15, p. 38; 16, p. 4379]. The low value of hydrogen activation energy (~ 0.1 eV) makes it difficult to conduct unambiguous experiments to identify the mechanisms of proton transfer in Si – SiO_2.

Numerous experimental results unequivocally state the presence of a significant number of proton-containing groups in the volume and on the surface of SiO_2 layers [15, p. 73; 17, p. 196; 18, p. 2528]. It is proved that H_2O molecules that diffuse through the SiO_2 layer in the oxidation process interact with the network of silicon – oxygen tetrahedra. On the SiO_2 surface, hydration reactions are real, accompanied by the rupture of overstrained silanoxone bonds and the formation of hydroxyl groups [17, p. 211]:



When H_2O molecules interact with oxygen vacancies in the oxide film, the formation of hydroxyl and hydride groups is possible:



Hydride groups lead to significant distortion of the structure of SiO_2 due to changes in the angles and lengths of bonds in silicon-oxygen tetrahedra.

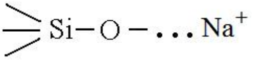
Electrophysical studies indicate the important role of these groups in the capture of charges transferred through the MOS-structure. In addition, the positive built-in charge differs significantly in the SiO_2 layers obtained by "wet" and "dry" oxidation of silicon. In general, proton processes affect the whole complex of electrophysical properties. The role of protons in the formation of a positive mobile charge in the oxide, which is responsible for the instability of the characteristics of the MOS-structures, is being intensively studied.

The question of the source of protons in MOS-structures also remains debatable. Si–OH and Si – H complexes, the concentration of which can reach $\sim 10^{20}$ cm^{-3}, have long been considered as such objects [15, p. 112; 17, p. 199]. However, experimental results show that coordinate-bound water $(H_2O)_k$ molecules have the highest proton activity [19, p. 37]. In MOS-structures, they will dissociate at the Si – SiO_2 and SiO_2 – metal boundaries. When applying an electric field, the generation of H^+ will take place by the electric field mechanism [20, p. 1535].

In general, oxide films are highly saturated with molecular water, hydroxyl and hydride groups, which in various ways are part of them. In addition, the available water molecules are bound to hydrated surfaces by α-Si hydrogen bonds [17, p. 173]. As Auger-studies show, due to surface activity in the presence of adsorbents, the chemical composition changes up to the formation of complex complexes. From the standpoint of such a "hydrogen" situation, the presence of a proton drift charge in Si – SiO_2 leads to the filling of traps under the action of an electric field (for example, associated with *LT*-maximum) and their subsequent devastation under the influence of external factors (thermal excitation, electric field, irradiation etc.). Moreover, the localization of H^+ ions on the bonds can lead to their stress and changes in spatial coordination up to the formation of asymmetric dipoles. The latter take part in polarization processes.

An important group of defects that significantly affect the functioning of MOS-devices are positive ions of alkali metals Na^+, K^+, Li^+, which in the operating modes of the devices become mobile. In particular, the concentration of Na^+ ions in the SiO_2 layers obtained by thermal oxidation reaches a value of $\sim 10^{18}$ cm^{-3}. Therefore, the moving charge of these ions in the structures of Si – SiO_2 is the cause of instability of the electrophysical parameters of field devices [21, p. 50].

Some Na^+ ions form ionic compounds with lean oxygen:



Thus, a modern interpretation of the experimental results of TSD-currents in Si – SiO_2 structures can be performed based on the mechanisms of bulk transport of ions through the dielectric layer and based on ideas about the existence of "classical" ion traps at the silicon – silicon dioxide interface. Moreover, the capture of ions does not change the electronic subsystem of the semiconductor. and are stationary. Moreover, the ratio of the concentration of stationary ions to the concentration of mobile ions is ~ 10^3 [11, p. 40]. With increasing ionic radius, the mobility of ions decreases according to the series: Na^+, K^+, Cs^+, etc. All alkali metals are a source of positive charge in the oxide. In contrast to the SiO_2 volume, where Li^+, Na^+, K^+ create a high donor level relative to the bottom of the silicon conduction band [23, p. 1232], ions located near the interface modify the surface states spectrum in the energy range corresponding to the silicon band gap.

In addition, such processes should take into account the effects of neutralization of ions and ion traps at the Si – SiO_2 interface, which are characteristic of such structures [23, p. 1234]. The peculiarity of such traps is the presence of long-range Coulomb and (or) dipole potentials, which leads to a field dependence of the emission rate of the particles trapped on them $\sim\exp(\alpha\varepsilon\gamma/kT)$, where ε is the external field, $1/2 < \gamma < 2/3$. It is shown that effective traps for positive mobile ions can be inhomogeneities of the interface of the type of dipole (charged) "spots".The presence of ions at the interface significantly modifies the spectrum of the surface states. In particular, in addition to increasing the density of states, a peak localized in the energy range ≈ 260 meV is realized at the tail of the spectrum due to the fluctuation potential. The number of states in it NS ≈ $3\cdot10^{11}$ $см^{-2}$, which is approximately equal to the number of neutral particles N_o.

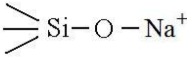
Therefore, it is likely to assume that the mobile ions of alkali metals and hydrogen, localized at the interface between radiation and shifted in polarization processes, will be partially neutralized due to the capture of electrons from the semiconductor substrate by tunneling. The number of such traps and the degree of their neutralization will determine the value of N_{max} in the *HT*-maximum. Moreover, the large width of the experimental spectrum associated with the *HT*-maximum is due to the localization at the interface of alkali metal ions in the ionized and neutral states, as well as the existence of several types of such ions and hydrogen-containing complexes.

Thus, the depolarization process of $Si – SiO_2$ structures may be limited to the processes of releasing ions from traps, the formation of neutral associates, their decay and the localization of mobile ions in lower energy traps. Moreover, the synchronous change of *LT*- and *HT*-maxima of TSD currents in the process of irradiation and repolarization indicates the common nature of the processes of devastation (delocalization) and subsequent localization of carriers in traps corresponding to the observed experimental maxima.The three-stage nature of the change in N_{max} with the time of irradiation for *LT*- and *HT*-maxima of TSD currents indicates the dominance at a particular stage of a certain mechanism of defect formation. In particular, the sharp decrease in N_{max} with the time of irradiation in the first stage of the *HT*-maximum is accompanied primarily by the structural rearrangement of hydrogen-containing complexes in the amorphous SiO_2 network. Namely, instead of weak bonds such as SiH and SiOH, stronger ones are formed – Si – O. This leads to a significant decrease in the density of states (stage I) and increase the radiation resistance of the $Si – SiO_2$ structure as a whole (stage II). The last third stage is characterized by a significant accumulation of radiation damage and, as a consequence, coordination changes of the amorphous SiO_2 network, rearrangement of defective-impurity complexes of the $Si – SiO_2$ interfacial boundary and possible transformation of the structural tetrahedron SiO_4 (with the formation of new structural types, for example $Si – SiO_4 H_4$ [15, p. 178]).

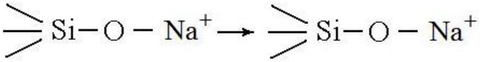
In this work, it was experimentally established that the height of the LT-maximum of the current in the TSD spectrum is directly proportional to the polarization voltage. Therefore, the dominant mechanism of formation of the electret state in this temperature range is the dipole mechanism. The probable mechanism of formation of such dipoles is the following. The release and subsequent migration of H^+ ions in the structural network of SiO_2 is accompanied by their localization at the bonds of Si – OH and Si – O complexes and violation of their symmetry with the formation of dipoles $Si^+ –OH^-$, $Si^+ –O^-$. Dipoles of this type are elements of the

SiO_2 structural network and have high rigidity. Therefore, they will not make a significant contribution to the polarization processes, which is confirmed experimentally for polarization in the region of the *LT*-maximum of the TSD current.Repolarization experiments show that trapped ions try to occupy lower energy traps (~ 0.8 eV) by migrating after thermofield excitation from higher energy traps (~ 1.0 eV). The consequence of this is an increase in the *LT*-maximum in the TSD spectrum with a simultaneous decrease in the *HT*-maximum.

Therefore, in the *HT*-maximum region, the Si – SiO_2 structure is characterized by a bulk-charge polarization mechanism involving alkali metal and hydrogen ions. The mechanisms of migration of hydrogen ions in the structural network of SiO_2 are discussed in detail in [8, p. 56]. As can be seen from Figure 3a, for the studied Si – SiO_2 structures two cycles "polarization-repolarization" are required in order to completely transfer positive ions located at the interface at the dielectric to the field electrode on SiO_2.The migration of alkali metal ions into the region of *LT*-traps, where hydrogen ions are localized, leads to the formation of various hydrogen-containing complexes involving silicon, oxygen and alkali metal, which have dipole properties. One of the variants of dipole formations that can take part in polarization processes in the region of *LT*-maximum are complexes with bound Na in the form:

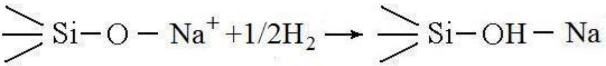


Moreover, such a complex under the action of irradiation is a source of Na^+ ions by the reaction:

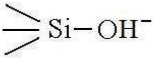


migrating to the area of LT-traps.

In addition, the probable substitution reaction of Na→H involving molecular hydrogen:



and the formation of a dipole



and the release of internodal Na. The latter is easily ionized, because its level lies at a distance of 1.7 eV from the bottom of the SiO_2 conduction band [6, p. 112].

5. Conclusions

1. In the electronic subsystem of the heterogeneous structure of Si – SiO_2, charge self-organization is realized by the redistribution of charges, which corresponds to the minimum value of the electronic entropy component of the system. Thermally stimulated depolarization is an effective methodology for the study of such processes.
2. The regularities of the TSD current spectra of the original and X-irradiated Si – SiO_2 structures have been investigated experimentally. Two characteristic maxima on the dependences *j (T)* were revealed: in the region 360K (LT-maximum) and 450K (HT-maximum), the values of which change synchronously in the process of irradiation.
3. It is established that the "polarization-depolarization" cycles of pre-irradiated Si – SiO_2 structures completely change the spectrum *j (T)*. Moreover, the nature of the TSD spectrum is determined by the temperature of the cycle. In particular, HT-repolarization (not more than two cycles) leads to the elimination of the HT-maximum observed in the original and irradiated structures of Si – SiO_2, with a simultaneous increase in the *LT*-maximum.
4. Using Fredholm's equations of the first kind, which describe the experimental dependences of *j (T)*, the energy distributions of the densities of the trap states that form the observed maxima are calculated. The activation energies of the respective centers and their frequency factors are estimated.
5. The kinetics of the change in N_{max} –the maximum value of the density of states in the region of characteristic maxima with irradiation time was studied. Significantly different nature of N_{max} behavior for *LT*- and *HT*-maxima was revealed. Possible mechanisms of such behavior are analyzed. The interpretation of the experimental regularities of *j (T)* TSD curves is based on the model of classical ion traps at the Si – SiO_2 interfacial boundary and the mechanism of bulk transport of H^+, Na^+ ions through the structural network of the SiO_2 dielectric layer.

6. Based on experimental results and modern model ideas about the main types of structural defects in the SiO_2 volume and at the Si – SiO_2 boundary, a conclusion is made about the dominance of the dipole mechanism of polarization of Si – SiO_2 structure in the *LT*-maximum region and volume-charge in the *HT*-region. maximum. The nature of dipoles that determine the polarization state within the *LT*-maximum is discussed.

7. It is advisable to analyze the charge self-organization of thermodynamically non-equilibrium systems from the standpoint of an open thermodynamic system. When transitioning to a thermodynamically balanced state, such a process has as its goal not only the achievement of neutrality of the structure, but mainly the realization of a thermodynamically balanced state with minimal entropy.

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