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# Electron states at the Si-$SiO_2$ boundary (Review)

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**Abstract.** This review is aimed at analysis of the system of discrete and continuously distributed boundary electron states (BES) on (111) and (100) silicon surfaces in the Si-$SiO_2$ structures prepared mainly using thermal oxidation of silicon. Used here are literature data as well as results obtained by authors when studying the temperature and electric field dependencies of the capacitive photovoltage. It has been ascertained that the BES system consists of a continuous U-like distribution in the silicon forbidden gap and from the discrete BES as well. There developed are two discrete BES in the thermally oxidized Si(111)-$SiO_2$ structure, while in the Si(100)-$SiO_2$ structure – four ones. These results well coordinated with ESR investigations were obtained using the method of temperature dependencies for capacitive photovoltage without application of an external electric field. As shown, application of various electric-field methods enables to determine only effective parameters of discrete and especially continuously distributed BES, which depend on the temperature of measurements, silicon resistivity and conditions of preparation of the Si-$SiO_2$ boundary. Considered are the features of pre-oxidation treatment of the silicon surface and its oxidation, the character of the intermediate layer between Si and $SiO_2$, and the influence of such external factors as annealing in various ambient atmospheres, irradiation and high electric fields as well.

**Keywords:** electron states, conductivity.

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## 1. Introduction

Electron states at a surface (interface) of solids were predicted in theoretical works by Tamm [1] and Shockley [2]. For the first time, these states were experimentally observed in the experiments made by Shockley and Pearson [3] who tried to influence with external electric field on the conductivity of Ge and $Cu_2O$ thin films, *i.e.*, to realize the idea of metal-dielectric-semiconductor (MDS) transistor. Originally, there was a failure in creating this transistor, which was related to strong screening the electric field by surface states, but the method providing the influence of the external electric field on the semiconductor conductivity later named as "field effect" found its wide applications in studying the system of surface (boundary) electron states (SES or BES) [4-6].

The idea of MDS-transistor was realized only after a considerable decrease in the density of electron states on the silicon surface by growing here an oxide layer due to high-temperature oxidation of silicon in oxygen atmosphere [7, 8]. This thermally grown oxide layer not only decreased the density value of BES at the boundary oxide-silicon ($SiO_2$-Si) by two – three orders, but appeared to be rather perfect dielectric layer, which, after covering this layer with a metal one, provided creation of the unique system – metal-oxide-semiconductor (MOS) successfully functioning for more than forty years in various devices of silicon electronics (transistors, varicaps, integrated circuits, CCD, *etc.*). Therefore, a huge amount of works (see, *e.g.*, [9-14]) were devoted to investigations of thermally oxidized silicon surface as well as to that after applying various methods for deposition oxide and other dielectric films onto this surface.

Despite the relatively low density of BES at the Si-$SiO_2$ boundary, which allows the external electric field to change the charge carrier concentration in the sub-surface area of the silicon MOS system, these BES, however, exercise a negative influence on operation efficiency of MOS devices. For example, BES increase the noise of transistors and integrated circuits based on MOS-systems, decrease the efficiency of charge transfer in CCD as caused by generation-recombination

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processes with BES participation (especially in CCD without a hidden transfer channel), promotes degradation of MOS-systems operating at high voltages and radiation of various types [9-14]. Therefore, a considerable part of works is devoted to investigations of the nature of BES at the boundary Si-$SiO_2$, determination of their parameters, as well as to changing the latter due to the influence of various technological factors, namely: conditions of a pre-oxidation treatment, technology of thermal oxidation and post-oxidation annealing in vacuum or some gas atmosphere. There investigated are BES parameters after various mechanical strains at the Si-$SiO_2$ boundary and high electric voltages as well as radiation exposures applied to the MOS-system. All these investigations are aimed at the BES nature, understanding of which will enable to eliminate these states or, at least, to reduce their influence to some minimum.

Predominant majority of methods to investigate the BES system is based on applying an external electric field to the boundary Si-$SiO_2$, which enables to determine BES parameters via measurements of the surface capacity, conductivity or photovoltage [9] due to changes in filling the boundary states with charge carriers. The external field is also applied when using the methods allowing to measure temperature dependencies of the surface capacity (the Gray-Brown method [15] and in the method of deep-level transient spectroscopy (DLTS) [16]. In our opinion, in these investigations studied is not only the system of the so-called fast BES but also partly the electron states located in the oxide film and, first of all, in its junction layer due to various mechanisms of electrotransfer between these electron states and bulk silicon, which is inherent both to electrons and holes. It complicates interpretation of experimental results and determination of BES parameters by using these data.

In [17-21], to study the BES system we offered the method for measuring temperature dependencies of the surface (capacitive) photovoltage, when the external electric field was not applied to the system Si-$SiO_2$. It enables to determine parameters of fast BES located at the silicon substrate. The obtained results are in good agreement with the data of investigations of paramagnetic centers in the silicon substrate, which was obtained using electron spin resonance (ESR) [22]. Performed simultaneously investigations of the photovoltage dependence on the value of the external electric field applied to the system Si-$SiO_2$ at various temperatures showed that in this case determined are the parameters of effective BES located both on the silicon substrate and in the $SiO_2$ layer [19, 21]. In this work, we analyze the results of investigations of the BES system that are obtained by us as well as numerous authors using the structures Si(100)-$SiO_2$ и Si(111)-$SiO_2$. Besides, we have briefly considered the response of the BES system on various actions applied to the Si-$SiO_2$ structure.

## 2. Preparation of the Si-$SiO_2$ system by using thermal oxidation of silicon

In relation with the tendency to increase the density of MOS-structures located on the unit of IC area, dimensions of MOS-structures in microelectronics are gradually lowered, which requires obtaining a thin (unities or tens of nanometers) gate insulator $SiO_2$ layer with a defectless structure [14]. Therefore, there formed rather hard requirements to the process of preparing the thermally oxidized Si-$SiO_2$ system. A considerable attention is paid to pre-oxidizing treatment of silicon plates, which mainly determines quality of the sub-gate $SiO_2$ layer. The oxidized silicon surface should possess no structural defects, be close to atomically smooth surface and contain no harmfull impurities (metal, carbon, *etc*.). Managed to realize something like to this surface by using several steps in liquid chemical treatment of silicon plates [23, 24]. The prepared by them surface was covered by the hydrogen monolayer and possesses a number of advantages over the atomically clean surface prepared and kept in super-high vacuum [23] not only from the viewpoint of more simple and convenient technology for making IC but also in relation to its higher cleanness and structural perfection as compared to the atomically clean surface prepared in vacuum. At first, silicon plates cut from monocrystalline ingots are treated with chemical-mechanical polishing in alkaline solutions (KOH or NaOH) to eliminate mechanical damages in the surface area that arise during the cutting process and to provide a flat polished surface. The following treatment is carried out using highly pure chemical reagents and deionized water to avoid contamination of the plate surface with harmful impurities, especially metal ions that are adsorbed by silicon [25].

One of the reliable ways to clean the plate surface from metal impurities and hydrocarbons is ten-minute treatment of them in the mixture $H_2O_2$:$NH_4OH$:$H_2O$ = 1:1:5 at 80 °C with the following rinse in deionized water (RCA treatment) [23]. At the following stage, they use various methods for slight preliminary oxidation of the plates (with chemical reagents, thermal processing in $O_2$ atmosphere or photooxidation in ozone atmosphere). This stage is aimed at oxidation of the subsurface layer containing structural defects after chemical-mechanical polishing, with the purpose of its following scalping. The scalping of this oxidized layer can be performed in water HF solutions with various concentrations (possibly with $NH_4OH$ additions) [23, 24], or in solutions of $NH_4F$ [23] as well as $HBF_4$ [26].

It was found that after treatments in HF, $NH_4F$ or $HBF_4$ silicon surface is protonized and possesses remarkable properties. Using various methods, namely, IR spectroscopy, scanning tunnel microscopy, low electron diffraction, photoelectron spectroscopy, ellipsometry, electron energy loss spectroscopy, *etc*., it was revealed that this silicon surface is passivated with

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hydrogen, contains hydrides of various types (Si-H, Si-$H_2$, Si-$H_3$) and is close to the atomically smooth one, with Si-H bonds being dominant on even parts. Si(111) and Si(100) surfaces are not reconstructed, do not contain superlattices from surface silicon atoms as it is usually observed at atomically clean surfaces prepared in vacuum. These hydrogen-passivated surfaces are hydrophobic [23, 24] and are not oxidized for a long time in dry oxygen and water that does not contain dissolved oxygen. The shelf time under ambient conditions for this surface can exceed several hours and is rather sufficient to transfer silicon plates into the chamber for thermal oxidation.

Creation of hydrogen-silicon bonds after treatments in HF, $NH_4F$ and $HBF_4$ instead of the silicon-fluorine ones seemed unexpected at the very beginning as the Si-F bond energy is close to 6 eV while that for the Si-H bond is 3.5 eV [23, 24]. A reasonable explanation for the process of protonized Si surface formation was offered in [23, 24, 28]. In the Si-F bond, the electron is mainly shifted from the Si atom to the F one ($\delta = 0.7$), while in the Si-H bond this transfer is much weaker ($\delta = 0.18$). As a result, $SiF_4$ molecules created first on the silicon surface are easily picked off the substrate silicon atoms due to solvation by water molecules, while these silicon atoms, in their turn, are profitably bound to hydrogen. However, after treatments of silicon in above mentioned fluorine acids there remain fluorine-hydrogen silicon compounds on its surface (*e.g.*, $SiH_2F_2$, $SiHF_3$), which requires short-time (less than 10 s) processing of these silicon plates in deionized water (without dissolved oxygen, as a rule) in order to provide complete elimination of fluorine compounds and creation of surface passivated only with hydrogen. It is noteworthy that the treatment of silicon surface in concentrated HF solutions (with low pH) results in more rough protonized surface than that in diluted HF solutions or in $NH_4F$ and $HBF_4$ solutions. Usually, in industrial conditions used are the following solutions: HF:$NH_4F$ = 1:7 or 40 % $NH_4F$ with pH = 5 and 7, 8 [23].

When placing protonized silicon plates into the chamber for thermal oxidation, hydrides are easily desorbed with increasing temperature. Thermal desorption of monohydrides is observed at 200 °C, dihydrides – at 400 °C and trihydrides – at 550 °C [23 ]. There exist various methods to prepare $SiO_2$ films [9-14]. However, the only thermally grown film is suitable for preparation of sub-gate dielectric. Earlier, to prepare it various technologies were used, too. For example, to neutralize various impurities easily diffusing in $SiO_2$ (in particular, sodium), these impurities being accumulated at the boundary Si-$SiO_2$, used were the technologies with addition of chlorine, phosphorus, lead [9]. At lower temperatures, $SiO_2$ layers with an adequate thickness were realized by addition of vapor into oxygen atmosphere. However, in recent years after reaching a technological purity when growing the $SiO_2$ layer, used is oxidation in dry oxygen that does not contain any impurities, as the latter beside a positive influence provide the negative one on the $SiO_2$ properties as well as on operation of MOS-structures in some cases.

Currently, thin films of $SiO_2$ gate insulator are grown in dry $O_2$ atmosphere within the temperature range 800 to 950 °C. As it was ascertained in [29], the most resistant to electric breakdown are the films oxidized at 850 °C independently from their thickness within the interval 3.5 to 5 nm. However, despite the more than 40-year period of successful applications of $SiO_2$ films as a gate insulator, the works to develop their preparation technology are in progress. So, for instance, some authors managed to prepare $SiO_2$ films with good parameters in dry $O_2$ at lower temperatures due to using ultra-violet (UV) [30] or excimer lamp radiation [31]. Although in the latter case the oxidation temperature was only 250 °C, the breakdown field reached $(7...10)\cdot 10^6$ V/cm, the films possessing the low density of the built-in positive charge. $SiO_2$ films prepared with UV radiation in dry oxygen at 600 – 900 °C possess a higher breakdown voltage, lower leakage currents and trap levels for holes when injecting them into the films as compared to the $SiO_2$ films obtained after their standard oxidation in dry $O_2$. Taking into account that structural and electric defects at the Si-$SiO_2$ boundary are caused by structural mismatch between Si and $SiO_2$, authors of [32] offered the method to realize stationary oxidation of silicon when the quantity of these defects is reduced to minimum. As the growth of the $SiO_2$ film takes place due to diffusion of oxygen through the previously created $SiO_2$ film [9], to keep oxidation stationarity it is offered to regulate either the oxidation temperature or the partial oxygen pressure.

## 3. Study of electron states at the Si-$SiO_2$ boundary

The most widely spread methods to investigate BES system at the boundary Si-$SiO_2$ are voltage-capacity $C(V)$ measurements, DLTS as well as studying the dependencies of the transverse conductivity in MOS-structures (impedance active component) in various frequency ranges $G(\omega)$-$V$ [9-14, 22, 33-36]. The $C(V)$-method enables to determine BES concentration and their energy-scale location inside the silicon forbidden gap, while DLTS and $G(\omega)$-$V$ methods, in addition, provide determination of the capture cross-section for majority carriers by BES, but to spread the investigation over the whole forbidden gap it is necessary to consider both *n*- and *p*-Si.

Most of the investigations were made using thermally oxidized structures Si(111)-$SiO_2$ and Si(100)-$SiO_2$. As usual, the Si(100)-$SiO_2$ structure possesses lower BES concentration, smaller built-in positive charge inside the $SiO_2$ film at the boundary and higher performances of MOS-systems based on it, therefore it is this structure that is used in IC production [9-14]. Although application of different methods to the same structure often results in different figures, it is possible

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to make some general conclusion about the BES system. It is ascertained that there is a common background of the continuous U-like BES distribution inside the silicon forbidden gap with increased concentrations near the edges of v- and c-bands. The BES concentration in this U-like distribution can change within wide limits from $1\cdot10^9$ up to $1\cdot10^{13}\,cm^{-2}eV^{-1}$ in dependency on technology of manufacturing the $Si$-$SiO_2$ structure. Besides, the above methods allows to found discrete levels below and above the middle of the silicon forbidden gap $E_i$ with concentrations within the range $1\cdot10^{10}$ to $1\cdot10^{13}\,cm^{-2}eV^{-1}$, which can be observed in the background of the U-like distribution as broad peaks [22, 33-36]. Maximums of these BES peaks both for Si(111)-$SiO_2$ and Si(100)-$SiO_2$ structures are located at 0.3 and 0.85 eV above the edge of silicon v-band [33-36].

In parallel with electric investigations of the BES system, in works [22, 33, 34] performed was studying the electron-spin resonance (ESR) in these Si-$SiO_2$ structures. Using the structure Si(111)-$SiO_2$, the authors of [33] revealed the ESR signal from the so-called $P_b$ center, comprehensive investigations of which [22] enabled to ascertain that it is located at the silicon surface and is a defect represented by a boundary silicon atom related to three Si atoms from the layer below, while one of its dangling bonds is oriented along the perpendicular to (111) plane. The $P_b$ center is designated as $Si_3{\equiv}Si\bullet$ defect. As it was shown by investigations of dependencies of the $P_b$ center ESR signal on the electrical voltage applied to the MOS-structure, the ESR signal is decreased when the Fermi level at the silicon surface is located closer than 0.3 eV to the v-band and further than 0.85 eV from it. In the former case the defect $Si_3{\equiv}Si\bullet$ loses the unpaired electron and become positively charged, while in the latter case it catch one electron more and become negatively charged. Both positively and negatively charged $P_b$ centers do not yield the ESR signal. Juxtaposition of ESR and DLTS results shows that the $P_b$ center is an amphoteric defect that creates two levels in the silicon forbidden gap, the distance between them being close to 0.55 eV and serving as an effective correlation energy for the centers with broken bonds at the boundary Si-$SiO_2$. It is well confirmed by simultaneous decrease of two peaks in the BES density determined with DLTS and the concentration of ESR centers when annealing MOS-structures in vacuum for 15 min within the temperature range 150 – 350 °C. The annealing at 450 °C (30 min) results in full decay of these ESR centers, concentration of which before this processing was $1.5\cdot10^{12}\,cm^{-2}$ [33].

Although the investigations of $C(V)$-dependencies [34], the $G(\omega)$-$V$ ones [35], both of these dependencies in combination with DLTS [36] by using the Si(100)-$SiO_2$ structure yield the positions of discrete BES density peaks inside the forbidden gap practically the same as for the Si(111)-$SiO_2$, ESR investigations of the Si(100)-$SiO_2$ boundary reveal two paramagnetic centers: $P_{b0}$ и $P_{b1}$ [34]. While the $P_{b0}$ center is identical to $P_b$ center at the (111) surface and also creates levels at the distance 0.3 and 0.85 eV above the v-band edge, the $P_{b1}$ center creates levels at the distances 0.45 and 0.80 eV above v-band and possesses the correlation energy value only 0.35 eV. For a long time, the nature of the $P_{b1}$center remained unclear and was under discussion. It was assumed, for example, that it is a center of $Si_2O{\equiv}Si\bullet$ type [22, 34]. At last, in [37] it was ascertained that the $P_{b1}$ center like to the $P_{b0}$ center is the defect $Si_3{\equiv}Si\bullet$ where oxygen is not its part but the broken bond of this defect has another orientation relatively to the (100) surface, namely, it is directed at the angle 20° to the axis ⟨011⟩. Thus, the only different orientation of the broken bond inherent to defects $Si_3{\equiv}Si\bullet$ yields different positions of energy levels in the silicon forbidden gap.

As it was noted in [34], one can observe a correlation between the energy distribution of BES and the total distribution of levels created by $P_{b0}$ and $P_{b1}$ centers. But the concentration of BES is approximately two times larger than the total concentration of $P_{b0}$ and $P_{b1}$ centers. It means that $P_{b0}$ and $P_{b1}$ defects represent only a part of BES, parameters of which are determined by the $C(V)$-method. As it is assumed in [13, 22], the reason of it lies in the possibility to control filling the electron states not only on the silicon surface where these states are created by $P_{b0}$ and $P_{b1}$ defects but electron states inside the intermediate layer of the Si-$SiO_2$ boundary, if using the $C(V)$-method. It is confirmed by our measurements of temperature (without any applied external voltage) and field (at various temperatures) dependencies for the surface photovoltage that will be analyzed in the following chapter. Moreover, our investigations enabled to separately determine parameters of energy levels created by $P_{b0}$ and $P_{b1}$ defects, which could not be done with $C(V)$, $G(\omega)$-$V$ and DLTS methods.

Concluding this chapter, it is reasonable to consider the question about the capture cross-sections by BES value of which can be determined by $G(\omega)$-$V$ [35] and DLTS [36] methods. As noted in [35], there are discrepant data in literature. For instance, applying the method $G(\omega)$-$V$ to the $n$-Si(100)-$SiO_2$ structure it was obtained that the capture cross-section reduces by two orders from $10^{-14}\,cm^2$ down to $10^{-16}\,cm^2$ for BES distributed from $E_i$ up to the c-band edge. For the $p$-Si(100)-$SiO_2$ structure, it was obtained that the cross-section by BES for holes changes from $10^{-16}\,cm^2$ down to $10^{-17}\,cm^2$ when the BES position changes between 0.25 and 0.05 eV starting from $E_i$. At the same time, the DLTS method yields in the independent from BES position value $10^{-14}\,cm^2$ for the capture cross-section of holes. Analyzing their own data obtained for the temperature range 300 – 100 K, authors of [35] made the conclusion that the capture cross-sections for electrons and holes do not depend on temperature and BES position inside the forbidden gap and are approximately equal to $10^{-16}\,cm^2$. By contrast, authors of [36] state that for holes the capture cross-sections have a considerable

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dependency on temperature. In our opinion, these differences in data both in quantitative and even in qualitative relations as regards to the capture cross-sections for carriers by BES in various BES positions and temperatures of measurements can be explained, on the one hand, by limitations of the used methods [36] and their incorrect use as well as, on the other hand, by the fact that these methods control not only BES on Si surface but inside the $SiO_2$ subsurface layer, that is dependent on $SiO_2$ technology.

## 4. Investigation of BES by surface photovoltage method

In our works, to study the BES system at thermally oxidized surfaces $n$-Si(100) [19, 21] and $p$-Si (100) [20] we used the method of the surface (capacitance) photo-voltage at a high generation level of electron-hole pairs in silicon excited by a light pulse capable to flatten energy bands at the boundary Si-$SiO_2$. It enabled to determine the boundary potential $\varphi_s$ in silicon in darkness (before illumination) under various temperatures and external electric fields when applying the latter to the Si-$SiO_2$ structure. It is noteworthy that the Dember photovoltage at high generation levels of charge carriers by the intense light pulse ($10^{21}$ quanta/cm$^2$s) does not play any essential role due to comparable values of diffusion coefficients as a consequence of electron-hole scattering [38].

Temperature dependencies of $\varphi_s$ within the range 300–100 K were taken using a cryostat with a measuring capacitor consisting of the sample with a mica insulator covered with a semitransparent conducting layer $SnO_2\langle Sb\rangle$. In the course of lowering the temperature, at its definite value we could observe the effect of photo-memory for $\varphi_s$ [25], therefore $\varphi_s$ measurements were performed by the first light pulse complying the procedure of cleaning out the surface traps from trapped minority charge carriers [39]. Electric field dependencies $\varphi_s(V)$ were measured under definite fixed temperatures within the range 300–100 K. The external voltage $V$ applied to the measuring capacitor was varied between +400 to −400 V. In this case, the measurements were carried out under illumination of the capacitor with the second light pulse in their train to eliminate the influence of the $\varphi_s$ photomemory effect by saturation of the traps with minority charge carriers created by the first light pulse as well as to avoid nonequilibrium arising in silicon at depleting voltages $V$ [40].

Depicted in Fig. 1 are the dependencies $\varphi_s(T)$ for thermally oxidized (curve 1) and chemically oxidized in $HNO_3$ (curve 2) surfaces $n$-Si(100). The curves 3 and 4 correspond to $\varphi_s(T)$ dependencies obtained after removing the oxide layers from surfaces in HF solutions. Negative $\varphi_s$ values correspond to existence of subsurface layers depleted with electrons. The growth of $|\varphi_s|$ with decreasing the temperature is caused by filling the BES with electrons as a consequence of the Fermi level shift

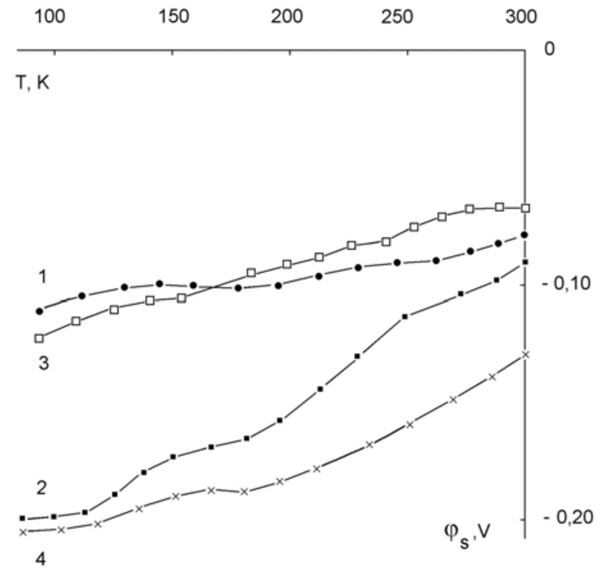


**Fig. 1.** Temperature dependencies of the surface potential for thermally (1) and chemically (2) oxidized silicon that was then treated in HF (curves 3 and 4, respectively).

to the c-band. The definite $\varphi_s$ value is corresponded by the charge $Q_{sv}$ in the silicon subsurface region that is equal to [9, 25]:

$$Q_{sv}= \sqrt{2}\, qn_iL\{\lambda^{-1}[\exp(q\varphi_s/kT) - 1] + \lambda[\exp(-q\varphi_s/kT) - -1] + q\varphi_s/kT(\lambda - \lambda^{-1})\}^{1/2}, \quad (1)$$

where $L = (\varepsilon\varepsilon_0 kT/q^2 n_i)^{1/2}$, $\lambda = n_i/n_0$, $n_0$ and $n_i$ are electron concentrations at the temperature $T$ inside the bulk of the studied and intrinsic silicon, respectively, $q$ is the electron charge, $\varepsilon$ is the silicon dielectric constant, $k$ is the Boltzmann constant, $\varepsilon_0 = 8.85\cdot10^{-12}$ F/m. The charge $Q_{sv}$ taken with the opposite sign is equal to the total charge $Q_s$ trapped in BES. When going from $Q_s(T)$ dependencies to the $Q(\psi_s)$ ones where $\psi_s = \varphi_b + \varphi_s$, the $\varphi_s$ value is measured and $\varphi_b$ value is determined for every $T$ from the condition $n_0 = n_i\exp(q\varphi_b/kT)$. The values $q\varphi_b$ and $q\psi_s$ are equal to the energy distance between $E_i$ and the Fermi level inside the silicon bulk and on its surface, respectively. The $Q_s(\psi_s)$ dependence allows to determine the density $N_{sf}$ of fast BES available at the silicon surface at various $q\psi_s$ (or energies $E$ inside the forbidden gap relatively $E_i$) in the following form:

$$N_{sf}(E) = |\Delta Q_s|/\Delta(q\psi_s). \quad (2)$$

Fig. 2 shows the obtained $N_{sf}(E)$ dependencies corresponding to surfaces characterized with the $\varphi_s(T)$ dependencies shown in Fig. 1. It is seen that the least BES density at the thermally oxidized surface (curve 1) that is corresponded to two observed BES density peaks at energies $E_i + 0.23$ and $E_i + 0.32$ eV with concentrations $6\cdot10^{10}$ and $3.4\cdot10^{10}$ cm$^{-2}$eV$^{-1}$. The largest BES density is observed on the chemically oxidized surface (curve 2).

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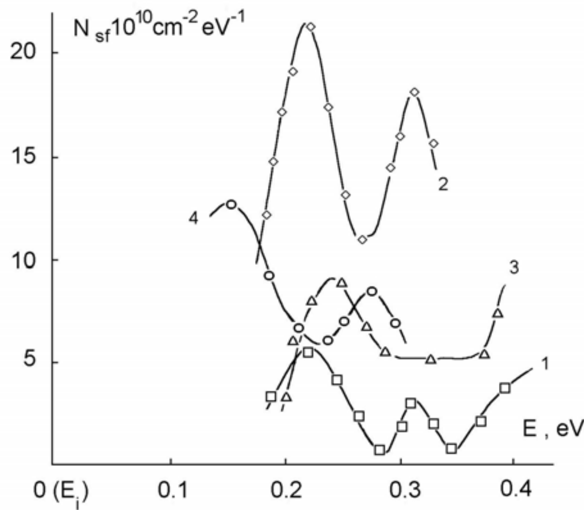


**Fig. 2.** Distribution of the density $N_{sf}$ of fast BES *vs* the energy above the middle of the silicon forbidden gap $E_i$. 1 and 2 denotes thermally and chemically oxidized Si surfaces; 3 and 4 – the same surfaces after their treatment in HF, respectively.

Also observed here are two density peaks possessing the same energy position as for the thermally oxidized surface within the accuracy 0.01 eV but with larger corresponding concentrations: $2.2\cdot10^{11}$ and $1.8\cdot10^{11}$ cm$^{-2}$eV$^{-1}$. The identical energy position of the found discrete BES both on thermally and chemically oxidized *n*-Si(100) surfaces is indicative of the same nature of defects causing their creation on these surfaces. We assume that these defects are $P_{b0}$ and $P_{b1}$ centers.

As seen from Fig. 2, after HF-treatment applied to the thermally oxidized surface the BES density grows a little (curve 3), while that of the chemically oxidized surface is lowered (curve 4). Also changed in this case are the energy positions of the BES density. The latter is obviously related with the fact that after HF-treatment, water rinsing and some exposure in ambient atmosphere, these are covered with hydrogen $SiH_x$ compounds and contain residual Si-F bonds as well as Si-OH and Si-O bonds creating in air, as it was shown earlier [23, 24]. Atoms H, F, O or OH-groups located near the $Si_3\equiv Si\bullet$ defects that remain non-passivated with hydrogen can result in changing the position of energy levels created by these defects [13]. Note that if the *n*-Si(100) surface thermally oxidized and then treated in HF to leave for aging in air, then already after 7 days the BES concentration increases and reaches values characteristic for the chemically oxidized surface, while in 22 days when a real relatively stable oxide is created [41, 42] it even exceeds these values [19]. In this case, the energy position of the BES density peak located closer to $E_i$ gradually becomes more close to $E_i$ with aging [19]. Thus, one can observe not only the growing concentration of $Si_3\equiv Si\bullet$ defects but also changing the energy positions of the levels created by them when aging the surface treated in HF and then acquiring the real oxide layer.

To determine BES parameters inside the bottom part of the silicon forbidden gap, in the work [20] we obtained temperature dependencies of the photovoltage inherent to thermally oxidized *p*-Si(100). We studied *p*-Si(100)-$SiO_2$ structures with thicknesses of $SiO_2$ equal to 90 and 3 nm. It was shown that in both cases we deal with discrete levels located below $E_i$ by 0.11 and 0.22 eV. Thus, the thermally oxidized (100) surface contains the system of discrete levels with the following energy positions: $E_i$–0.22, $E_i$–0.11, $E_i$+0.23 and $E_i$ + 0.32 eV. The energy positions of middle levels ($E_i$ – 0.11 and +0.23 eV) coincide with those of created by $P_{b1}$ centers developed in ESR investigations [34] with the accuracy 0.01 eV. The extreme levels ($E_i$–0.22 and +0.32 eV) are close to those created by $P_{b0}$ centers ($E_i$–0.26 and +0.29 eV, respectively [34]). This difference 0.03–0.04 eV between our results and those obtained in [34] can be related with worsening the accuracy of surface potential determination from $C(V)$-measurements when band bends are large. But note that the correlation energy value for the $P_{b0}$ center is the same both in our work and in [34].

Thus, the method of photovoltage temperature dependencies without applying any external electric field allowed to separately develop the levels created by $P_{b1}$ and $P_{b0}$ centers on the thermally oxidized (100)Si surface. Before our works, it did not manage to do that with various electric or photoelectric methods. Then was an opinion that $P_{b1}$ centers do not create levels in the forbidden gap, which could manifest themselves in electric measurements [43]. However, in the work [44] where spin-dependent recombination (SDR) of charge carriers at the Si(100)-$SiO_2$ boundary was investigated applying the variable voltage to a MOS-structure, it was shown that this recombination occurs through both $P_{b0}$ and $P_{b1}$ centers, *i.e.*, the latter are located in the silicon forbidden gap. However, to determine energy level positions for $P_{b0}$ and $P_{b1}$, as it was done in our work, the SDR method could not manage, because it yields very broad signal lines.

As it follows from the above results, the use of methods even with little (differential) voltages applied to the MOS-structure is accompanied with a partial capture of charge carriers by electron states in the oxide film, at least in its intermediate layer with silicon. An essential growth of this capture was also observed in our works [19, 21] where dependencies of the capacitance photovoltage were measured under various temperatures as a function of high Π-pulse voltage $V$ applied to the measuring capacitor possessing the specific capacitance $C_d$. In this case, to obtain the BES density distribution inside the silicon forbidden gap, we used the $\varphi_s(V)$ dependencies that allows to calculate the BES density for various $\varphi_s$ according to the formula [45]:

$$N_s(\varphi_s) = [C_d(dV/d\varphi_s - 1) - dQ_{sv}/d\varphi_s]/q \, . \quad (3)$$

As it was done above, $N_s(\varphi_s)$ dependencies obtained for a definite temperature allow to obtain the $N_s(\psi_s)$ ones or,

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what is the same, $N_s(E)$ dependencies. Shown in Figs 3 and 4 are the dependencies $N_s(E)$ for thermally and chemically oxidized *n*-Si(100) surfaces, respectively, measured within the temperature range 290 down to 130 K. For the thermally oxidized surface, the BES concentration $N_s$ within the energy interval –0.2...+0.2 eV relatively to $E_i$ does not depend on the temperature of measurements and lies within the limits $(2...4)\cdot10^{11}$ cm$^{-2}$eV$^{-1}$. The dependency of $N_s$ on temperature is observed within the range 0.2 to 0.5 eV above $E_i$. A sharp growth of $N_s$ at more high temperature begins at lower $E$ (or $\psi_s = \varphi_s + \varphi_b$). It takes place when to silicon surface one applies the electric fields capable to enrich the subsurface area with electrons and to rise $\varphi_s$. The $\varphi_s$ – values for which $N_s$ grows sharply are approximately the same at various temperatures. And the observed shift of the $N_s$ growth beginning into the side of higher $E$-values with increasing the temperature is caused by the growth of $\varphi_b$ from 0.28 eV at 290 K up to 0.47 eV at 130 K.

If comparing the dependencies $N_{sf}(E)$ and $N_s(E)$ (Figs 2 and 3) obtained for the same thermally oxidized surface by using two different approaches, one can see that, first, the character of the BES distribution differs: the $N_{sf}(E)$ dependencies possess a discrete structure, while the $N_s(E)$ ones show a continuous BES distribution. Second, the BES concentration determined using the $\varphi_s(T)$ dependencies is more than 10 times less as compared to $N_s$ determined from the $\varphi_s(V)$-dependencies at various temperatures. It is related with the fact that the $N_{sf}$ value determined in absence of external electric field is only equal to the concentration of true fast BES located on the silicon surface in the Si-$SiO_2$ structure. At the same time, when using the electric-field method to obtain the $N_s$ value one can observe supplementary BES located in the near-boundary (intermediate) area of $SiO_2$ film, as there is a considerable electric field promoting transfer of charge carriers between silicon and the oxide BES.

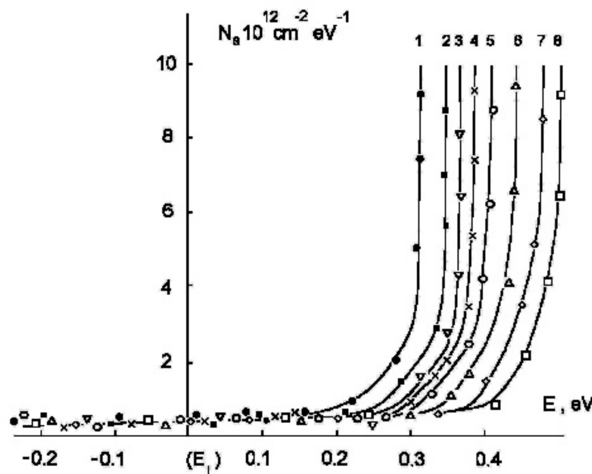


**Fig. 3.** Distribution of the effective BES density $N_s$ *vs* the energy for the thermally oxidized Si surface at various temperatures: 1 – 290, 2 – 270, 3 – 255, 4 – 230, 5 – 205, 6 – 185, 7 – 150, 8 – 130 K.

When inducing the charge $Q_{\rm ind}$ on silicon surface at the initial moment before changing the charge in BES, the electric field inside the oxide film $\xi_s$ is as follows:

$$\xi_s = Q_{\rm ind} / \varepsilon_d\varepsilon_0 = [Q_{sv}(\varphi_{so}) - Q_{sv}(\varphi_s)] / \varepsilon_d\varepsilon_0, \quad (4)$$

where $\varphi_{so}$ and $\varphi_s$ are the silicon surface potentials before and after application of an external electric field to it, respectively, $\varepsilon_d$ is the silicon oxide dielectric constant. When $\varphi_s > 0$, the charge $Q_{sv}$ is negative, while for $\varphi_s < 0$ it is positive.

According to formulae (1) and (4), the electric field in the oxide film $\xi_s$ is in proportion to $|q\varphi_s/kT|^{1/2}$ when the external field voltage depletes silicon with electrons. In our experiments, $\xi_s$ reaches $3\cdot10^4$ V/cm. A sharp growth of $\xi_s$ takes place, if one applies enriching voltages: $\xi_s \sim \exp(q\varphi_s/kT)$. In the case of low temperatures, this sharp growth is observed at high $E \equiv q\psi_s$ [46], as it follows from the formulae (1) and (4). Thus, there is a correlation between the dependencies $\xi_s(E)$ and $N_s(E)$ in the enriched region: the larger $\xi_s$ is corresponded by the larger effective BES density, $\xi_s$ and $N_s$ being dependent on the temperature of measurements. Effectively, the correlation between $\xi_s(E)$ and $N_s(E)$ explains the results of the work [47]. There, for the first time in investigations of the field effect (that is the influence of an external electric field on the subsurface conductivity of germanium and silicon), attention was turned to the correlation between dependencies of the charge in BES and that in the subsurface semiconductor region on $\varphi_s$ when changing the semiconductor resistivity and temperature of measurements.

Among various possible mechanisms of electron transfer between silicon and electron states in oxide [9, 10], an essential role can be played by the tunnel mechanism of transfer from the silicon c-band into oxide states located in the vicinity of the Si-$SiO_2$ boundary, if the voltages are enriching.

Immediately after applying the electric field to the Si-$SiO_2$ structure, the rate of tunnel filling with electrons some kind oxide states with the concentration $N_{to}$ can be expressed as

$$dn_{to} / dt \sim DC_{no}(N_{to} - n_{to})\, v_s\, n_s, \quad (5)$$

where $n_{to}$ is the concentration of electrons in oxide states, $C_{no}$ is the effective capture cross-section for electrons by these states, $n_s = n_o\exp(q\varphi_s/kT)$ is the electron concentration in the c-band near Si surface, $v_s$ is their thermal velocity, $D$ is the transmission coefficient for electrons in the space of the thickness $d$ between Si and oxide states, which is equal

$$D = D_0\exp\{-4/3\sqrt{2}\, m/\hbar\, [(U-E_n)^{3/2} - (U - q\xi_s d - E_n)^{3/2}]/q\xi_s\}, \quad (6)$$

where $D_0 \approx 1$, and $U$ is the height of the potential barrier at the Si-$SiO_2$ boundary, $E_n$ – the energy of tunneling electrons, $m$ – electron effective mass in oxide, $\hbar$ – the Planck constant divided by $2\pi$.

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As it follows from the formulae (5) and (6), in the case of enriching voltages electron tunneling into the oxide states grows considerably due to increasing $D$ and $n_s$ values. As seen from calculations, the latter factor is especially essential, because $n_s$ grows exponentially with $\varphi_s$. Electron tunneling results in a considerable growth of the effective BES density determined from the electric-field photovoltage investigations, while the true density of fast BES $N_{sf}$ determined from photovoltage temperature dependencies within the range 0.2 up to 0.4 eV above $E_i$ is more than ten times less in its magnitude (Figs 2 and 3). Note that when measuring the photovoltage temperature dependencies (without any external electric field) the silicon forbidden gap is studied in the regime of depletion of the surface with electrons. In this mode, electron tunneling from Si into oxide states does not take place via the absence of the electric field in oxide, which is capable to promote tunneling and due to low $n_s$ values.

As seen from Fig. 4, in the case of chemically etched in $HNO_3$ silicon surface the effective density $N_s$ considerably grows as compared to that for thermally oxidized surface. It is related both with a large quantity of defects creating electron states in the oxide film and with an increasing probability of charge carrier transfer between these states and silicon due to various transfer mechanisms [9, 10]. When removing the chemically oxidized film by etching in HF, $N_s$ values are considerably reduced at definite $E$ and $T$ values, which is indicative of the fact that just the states in the chemically oxidized film mainly contribute into determined effective $N_s$ values. Note that the $N_s(E,T)$ values were practically the same after etching both chemically and thermally oxidized films. Thus, as it follows from electric field photovoltage investigations at various temperatures, the determined distribution of the efficient BES inside the silicon forbidden gap depends both on the state of the oxide film on the silicon surface and on measurement temperatures as well as the silicon resistivity (parameter $\varphi_b$).

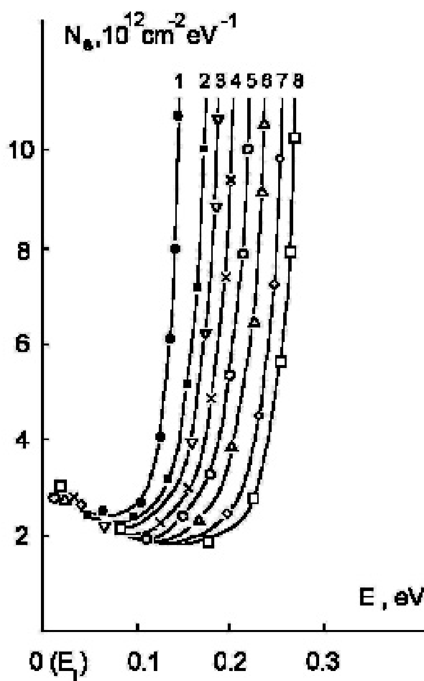


**Fig. 4.** Distribution of the effective BES density $N_s$ *vs* the energy on the chemically oxidized Si surface at various temperatures: 1 – 290, 2 – 270, 3 – 255, 4 – 230, 5 – 205, 6 – 185, 7 – 150, 8 – 130 K.

The latter inference allows to make the conclusion that improvement of MOS-transistor functions (that is a decrease of a harmful influence of BES) requires not only a structurally perfect Si-$SiO_2$ boundary with a low defect concentration both in it and the $SiO_2$ film but a moderate silicon resistivity of MOS-structures as well as lowered operation temperatures for MOS-transistors.

## 5. Intermediate layer at the Si-$SiO_2$ boundary and U-like dependency of the BES density

In the majority of works studying the structure and electrophysical properties of the Si-$SiO_2$ system, intimated is the presence of an intermediate layer between Si and $SiO_2$ , which consists of near-boundary Si and $SiO_2$ layers more or less smoothly transforming one to another and possessing properties that differ, respectively, both from those of Si bulk and $SiO_2$ [9-14]. For 40-year history, the thickness of the thermally grown insulating $SiO_2$ layer has been reduced from hundreds of nanometers to the values less than 4 nm [14]. In accord with these technological achievements, the thickness of measured intermediate layer has been decreased from 3...5 nm to parts of nanometer. As this takes place, one can note vanishing some its definite properties and domination of others. To study this intermediate layer, used was a powerful arsenal of various methods, namely: the optical ones (various methods of infrared (IR) and ultraviolet (UV) spectroscopy, monochrome and spectral ellipsometry, light electroreflectance, optical microscopy, *etc.*); X-ray methods (X-ray imaging, photoelectron spectroscopy); electron-beam methods (electron diffraction, Auger-electron spectroscopy, electron-energy characteristic loss spectroscopy, transmission electron microscopy, reflection electron microscopy); ion-beam methods (Rutherford back-scattering spectroscopy, mean energy range ion spectroscopy, secondary-ion mass-spectroscopy); scanning tunnel microscopy, electron-spin resonance, *etc*. [9-14, 25, 48]. The intermediate layer was investigated both directly in Si-$SiO_2$ structures with a various thickness of the $SiO_2$ film and in the course of thinning the $SiO_2$ film in a slowly etching HF solution or when sputtering it with an ion beam.

It was ascertained that the determined thickness of the intermediate layer depends both on the technology of the $SiO_2$ film preparation and on the methods of its investigations. Thermal oxidation of silicon stimulates

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break of Si-Si bonds (energy per one bond is equal to 1.97 eV) that is followed by creation of more fast Si-O bonds (energy per one Si-O bond in $SiO_4$ tetrahedron is equal to 5 eV). Energy released in these reactions promotes creation of structural defects in the silicon subsurface region possibly up to its partial amorphization. Besides, the silicon subsurface region is enriched with imbedded oxygen, concentration of which can exceed the solubility limit in silicon bulk [9]. In addition, one can also observe accumulation of various impurity atoms at the Si-$SiO_2$ boundary where they gather both from the silicon side and from the side of growing $SiO_2$ layer. Therefore, to create more perfect Si-$SiO_2$ boundary, technology of its preparation was advanced by elimination of impurity atom influence and reducing the amount of structural defects created in the silicon near-boundary region. It has been successfully realized providing super-high purity conditions for growing the $SiO_2$ layer, using super-high purity reagents, choosing an optimum temperature and regimes for silicon oxidation as well as post-oxidizing annealings [9-14]. But works in this direction are going on. For example, as noted in [30, 31], works to lower oxidation temperatures for silicon are carried out.

It was shown using the listed above methods that the $SiO_2$ film grown on silicon is amorphous but can include some microcrystalline inclusions, especially in the vicinity of the intermediate layer [9, 48]. The base of all the $SiO_2$ crystalline and amorphous modifications is formed by silicon-oxygen tetrahedra $SiO_4$, the bond length and valence angles of which does not practically depend on the type of modification and are equal to 0.16 nm and 109°, respectively [48]. In $SiO_2$ amorphous films, the short-range order is conserved, and angles between $SiO_4$ tetrahedra change within the wide range from 120 up to 180° with the maximum of their distribution close to 147°. In $SiO_2$ amorphous film bulk, $SiO_4$ tetrahedra mainly form 6- and 4-link rings, the 4-link ones being dominant in the vicinity of the boundary [49]. A smaller angle between tetrahedra is a characteristic feature for bridge bonds in these 4-link rings.

Availability of microcrystalline $SiO_2$ inclusions near the boundary was mainly observed in more thick $SiO_2$ films in insufficiently pure conditions for their growth, when various impurities (in particular, sodium atoms or ions [9]) become crystallization centers for $SiO_2$. Currently, they are absent in insulator $SiO_2$. However, the intermediate $SiO_2$ layer is enriched with silicon (or, in other words, depleted with oxygen). It is considered that there are suboxides of the following types $Si_2O_3$, SiO and $Si_2O$ near the boundary from the $SiO_2$ side, which is capable to explain oxygen deficiency. As it was ascertained in [50], where oxygen films with the thickness 2.4 nm were studied, the thickness of suboxide layer was only 0.2 nm, *i.e.*, the boundary between Si and $SiO_2$ is close to the very sharp one. These suboxides consist of Si-$O_x$-$Si_{4-x}$ type silicon-oxygen clusters ($1 \le x < 4$) [51] that possess angles in bridge Si-O-Si bonds less than those between silicon-oxygen tetrahedra in $SiO_2$ bulk, which manifests itself in red-shifted bands observed in IR spectra.

Besides, electrophysical and ESR methods found point structural defects in $SiO_2$ near-boundary region (for example, E-, S-, EH- and EX-centers) [9-13, 48, 52-54]. These centers serve as capture centers for electrons and holes and can manifest themselves in various electrophysical investigations of electron states inside the Si-$SiO_2$ boundary, in particular, when applying electric field to it, which has been considered by us above. Possible intrinsic defects in $SiO_2$ that can serve as capture centers for electrons and holes have been analyzed in [55]. In particular, electrons and holes can be captured by E′-center that is the $O_3{\equiv}Si\bullet$ defect. This defect is assumed to be responsible for appearance of the built-in positive charge in oxide near the Si-$SiO_2$ boundary in the course of silicon thermal oxidation [9]. Note that the built-in positive charge is inessential when the $SiO_2$ thickness is less than 4 nm [14]. The role of electron traps can be also played by proton-containing defects (*e.g.*, Si-OH and Si-H groups) [48], which is especially typical for oxides prepared in wet medium. Thus, there are specific intermediate regions both from the silicon and $SiO_2$ sides at the Si-$SiO_2$ boundary.

The intermediate region in the Si-$SiO_2$ structure is considerably affected by internal mechanical strains (IMS) [56-61]. There are two main reasons of IMS appearance, namely: i) structural mismatch between silicon and the growing oxide film, which results in compressive strains in oxide arising in the process of thermal oxidation, while in near-boundary silicon layers stretching strains (intrinsic IMS) take place; ii) difference between coefficients of thermal expansion for oxide and silicon ($5\cdot10^{-7}\,K^{-1}$and $3\cdot10^{-6}\,K^{-1}$, respectively), which yields in an increased level of IMS in the Si-$SiO_2$ structure when cooling it from the oxidation temperature to that of application (or the room one). The intrinsic IMS are approximately equal to 70 % of the total IMS value [59]. As the thickness of the $SiO_2$ film is usually much less than that of the silicon substrate, the IMS value in the $SiO_2$ film is essentially higher than in the substrate. The former reaches $(2–6)\cdot10^8$ Pa, while the latter is approximately $10^7$ Pa. This latter value is far from the ultimate stress limit $(2–4)\cdot10^9$ Pa [58], but is close to the beginning of the microflow process in silicon, which is realized in the case of thick $SiO_2$ films [60]. These strains in the silicon substrate are sufficient, at least, to create point defects at the silicon boundary and enhance this process when applying high electric voltages to the Si-$SiO_2$ structure or exposing it to various kinds of radiation [61, 62]. It is noteworthy that from the analysis of possible conjugation between Si and $SiO_2$ lattices as well as from experimental data [51], it follows that IMS at the boundary Si(111)-$SiO_2$ are higher than those at the Si(100)-$SiO_2$ boundary. As a consequence, there observed a larger amount of created point defects of the $P_b$ center type on the silicon surface with (111) orientation [22].

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After this consideration of intermediate layer properties at the Si-$SiO_2$ boundary and IMS inherent to it, let us turn to U-like background of BES density distribution in the silicon forbidden gap, on which the BES created by $P_b$ centers manifest themselves. The BES concentration in this U-like distribution also depends on technology of Si-$SiO_2$ structure preparation, but the nature of these BES differs from that of the BES created by $P_b$ centers. The former are usually observed near c- and v-bands of silicon and practically do not change, for instance, after low-temperature (up to 450 °C) annealings in vacuum, as it takes place with BES created by $P_b$ centers [22].

For the first time, notions about the nature of the U-like BES distribution were developed in the works [63, 64] by using the concept of a disorder available at the semiconductor-dielectric boundary. It was assumed in [64] that the reason of these BES appearance lies in considerable oscillations of effective charge values on Si and O atoms in the intermediate layer $SiO_2$, and this fluctuating charge yields in creation of this U-like distribution of BES on silicon surface, if using the theory of disordered systems [65]. The charge fluctuation on Si and O atoms is caused by fluctuations of angles in Si-O-Si bridge bonds of boundary silicon-oxygen tetrahedra $SiO_4$ and clusters Si-$O_x$-$Si_{4-x}$. This angle fluctuation arise in the course of Si-$SiO_2$ structure creation and is enhanced by IMS.

A direct confirmation of above considerations was obtained from the studying the boundary region of the Si-$SiO_2$ structure by using highly-resolving X-ray photoelectron spectroscopy [66]. The model explicated above is also supported by theoretical works [67, 68]. In [67], using the method of Bette lattices shown was that angle variations of Si-O-Si bonds at the boundary result in creation of BES density tails near c-bands of Si and $SiO_2$, while variations of Si-Si bonds available in the near-boundary oxide layer cause creation of the BES density tail near the Si v-band as well as tails in the $SiO_2$ forbidden gap. Using the same method, it was obtained in [68] that even ideal contact between silicon and oxide lattices cause state tails in the silicon forbidden gap near c- and v-bands.

In summary, it is worth to note that although these U-like distributed BES negatively effects on operation of MOS-devices, the deeper BES (created by $P_b$ centers) are rather more harmful as they supplementary serve as generation-recombination centers for electron-hole pairs.

## 6. Influence of external factors on the BES system

### *6.1. Annealings of Si-$SiO_2$ structures*

Usually, when creating the MOS-structure, deposition of the metal layer (or polysilicon) is followed by their annealing at relatively low temperatures (< 450 °C). This annealing in vacuum provides good adhesion of the metal layer to $SiO_2$ . Besides, annealing at relatively low temperatures decreases IMS in the Si-$SiO_2$ system to some extent, eliminates many structural defects in the intermediate Si-$SiO_2$ layer, shortens its thickness, and reduces the BES concentration as well [9]. As it was mentioned above, in [33] BES created by $P_b$ centers practically vanished after low-temperature annealings in vacuum. In contrast, the annealing in vacuum at higher temperatures (> 600 °C) more significantly decreases IMS at the boundary owing not only to changing the Si-O-Si bond angles in the intermediate layer but to creation of the point defects of the $P_b$ center type on the silicon surface, *i.e.*, one can observe a growth in the BES concentration [69]. Besides, high-temperature (> 700 °C) annealings in vacuum cause degradation of the oxide film via creation of point defects in it, which can be determined using the ESR method [53]. Thus, to reduce the BES concentration one should use the only low-temperature annealings in vacuum. The possible mechanism providing the decrease in the BES concentration due to neutralization of $P_b$ centers in this case was offered in [70]. It was shown being based on theoretical calculations that passivation of silicon broken bonds caused by creation of Si=O double bonds in conditions of oxygen deficiency (vacuum annealing) stimulates displacement of levels created by $P_b$ centers from the forbidden gap into extended bands, which means that BES disappear from the forbidden gap.

Taking into account that in some cases it is necessary to do high-temperature annealings of the Si-$SiO_2$ structure (for example, to reduce the concentration of the built-in positive charge in oxide) in [71] they investigated the high-temperature annealing (1000, 1100 or 1160 °C) of Si-$SiO_2$ structures not only in vacuum but in various gas atmospheres (He, Ne, Ar, $N_2$) as well. It was ascertained that the vacuum annealing increases the concentration of BES stemming from $P_b$ centers and results in degradation phenomena in $SiO_2$, namely: an increased conductivity of $SiO_2$ even at low voltages applied to the MOS-structure; enhanced sensitivity of $SiO_2$ to radiation that generates a higher concentration of hole traps. Annealings in Ne, Ar and $N_2$ atmospheres were able to eliminate some of the considered above negative phenomena inherent to the structure after the vacuum annealing, however, the best result was obtained for He atmosphere. The annealing in He resulted in practically full elimination of above negative phenomena. The authors assumed that it takes place due to embedding the small-size He atoms into oxide and especially into the Si-$SiO_2$ boundary, which prevents chemical reactions between Si and $SiO_2$ as well as creation of point defects at Si-$SiO_2$ boundary.

A large amount of works (*e.g.*, see [72-78]) were devoted to passivation of $P_b$ centers caused by the annealing of Si-$SiO_2$ structures in hydrogen atmosphere providing disappearance of levels related to BES stemming from $P_b$ centers. In [72, 73] studied was the passivation kinetics of $P_b$, $P_{b0}$ and $P_{b1}$ centers at the Si-$SiO_2$ boundary in the course of the annealing in $H_2$ atmosphere within the temperature range 213 – 234 °C.

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It is assumed that passivation of $P_b$, $P_{b0}$ and $P_{b1}$ centers is caused by the reaction $Si_3{\equiv}Si\bullet + H_2 \rightarrow Si_3{\equiv}SiH + H$. Values of the activation energy for this reaction are practically the same for $P_b$, $P_{b0}$ and $P_{b1}$ centers and are equal to 1.51, 1.51 and 1.57 eV, respectively, which is not a surprise as $P_b$ and $P_{b0}$ centers located accordingly on (111) and (100) silicon surfaces are identical, while the $P_{b1}$ center on (100) surface differs from $P_{b0}$ centers only by the orientation of the silicon atom broken bond. $P_bH$, $P_{b0}H$ and $P_{b1}H$ complexes created in the course of passivation are rather unstable. They decay during the annealing in vacuum at temperatures ≥ 500 °C, and are very unstable under radiation influence as well as high electric voltages applied to MOS-structures [74]. In [75], authors offered a theoretical model for thermal dissociation of the above complexes in (111) and (100) $Si$-$SiO_2$ structures taking into account diffusion of hydrogen atoms and molecules into $SiO_2$ provided by annealings in vacuum within the temperature range 480 – 700 °C. This model has a good accordance with experimental data. It is essential to note that the activation energies for hydrogen deliberation from $P_bH$, $P_{b0}H$ and $P_{b1}H$ complexes are equal to 2.78, 2.86 and 2.91 eV, respectively.

There are some distinctions in behavior of atomic hydrogen H as compared to the molecular one $H_2$ if regards to $P_b$ centers [74, 76, 77]. As shown in [76], in contrast to $H_2$ the atomic hydrogen is able not only to passivate but also depassivate silicon broken bonds even at room temperatures due to the following reactions: $P_b$+H→$P_b$H and $P_b$H+H→$P_b$+$H_2$. It was ascertained in [77] that if at 400 °C atomic hydrogen passivates BES like the molecular one does, then at room temperatures (when $H_2$ is passive) it recovers the same defects that were present before their passivation with H or $H_2$. Besides creation of fast BES related mainly with silicon broken bonds, atomic hydrogen also forms traps (slow states) inside the $SiO_2$ film. In this case, the defects created by atomic hydrogen at the boundary and inside $SiO_2$ possess similar properties as compared to those of defects created by radiation as well as injected hot carriers [77]. Thus, in our opinion, passivation of silicon broken bonds with hydrogen (H and $H_2$) is not a reliable method to eliminate them. Moreover, as it was shown in [78], the annealing of the $Si$-$SiO_2$ structures in $H_2$ atmosphere at 450 – 800 °C results in creation of a considerable (up to $10^{13}$ cm$^{-2}$) positive charge inside the $SiO_2$ film that is caused by the centers not providing any ESR signal.

In some relation, promising are the annealings in nitrogen-containing media ($N_2$, NO, $N_2O$). Processes that take place in this case yield in creation of $Si/SiO_xN_y$ structures and are enlightened in more details in the review [14]. Our purpose is only to note some positive properties acquired by the $Si$-$SiO_2$ structure after nitrogening. As shown in [79], the concentration of $P_b$ centers sharply drop after the annealing of the Si(100)-$SiO_2$ structure in NO (from $2\cdot10^{12}$ down to $< 1\cdot10^{11}$ cm$^{-2}$). It takes place due to NO penetration through $SiO_2$ to the $Si$-$SiO_2$ boundary with simultaneous appearance of built-in N and O atoms in it, which results in passivation of $P_b$ centers without "harmful" effects of hydrogen. At the same time, dielectric properties of $SiO_2$ are kept.

As it was ascertained in [80], after annealing the Si(100)-$SiO_2$ structure in $N_2$ the nitrogen atoms embedded into the boundary lower IMS in the structure and increase stability of the boundary to trap generation during current loads. There observed some improvement of the Si(100)-$SiO_2$ boundary after annealing the sample at 900 °C $N_2$ atmosphere [81], namely, lowered is its roughness related to oxidation dynamics of (100) surface (the Si(111)/$SiO_2$ boundary is more smooth, and the annealing in $N_2$ has no effect on it). Note that roughness increases the BES concentration and built-in charge in oxide [82].

### *6.2. Radiation effects on the BES system*

The existence of the intermediate layer containing IMS cause increased sensitivity of the $Si$-$SiO_2$ structure to various radiation effects [61, 62]. The structural transition from Si to $SiO_2$ through the intermediate layer where chemical bonds between atoms are strained and weakened results in a decreased threshold for defect creation as well as increased rate defect generation. In contrast to creation of radiation defects inside the Si or $SiO_2$ bulk, specificity of their creation at the boundary $Si$-$SiO_2$ is influenced by the following factors: elastic strains before radiation and their relaxation in the course of radiation; capability of atoms (ions) to move inside the boundary during radiation and after it; presence of electric fields inside the boundary (either applied from outside or caused by the built-in charge inside oxide) that like to IMS influence on atom (ion) displacements and, in such a manner, enhance structural reconstructions of the boundary as well as change the rate of chemical reactions in it.

Radiation actions on solids are caused by ionization losses of the energy or by elastic collisions of particles (photons) from the exposing beam interacting with atoms of solids [62]. When irradiation is realized by light quanta with various wavelengths, electrons, X-rays or gamma-quanta, the main channel for energy losses is ionization of atoms. In the case of ion-beam irradiation, besides atom ionization the dominant part of the ion energy is spent for elastic collisions with atoms that are shifted from their regular positions, especially when using more massive ions. Respectively, consequences of actions made by different kinds of radiation can be different.

If using radiation capable mainly to ionize atoms in conditions of moderate intensities of particle (quantum) fluxes and their energies, it is possible to realize the case when the structural reconstruction of the boundary stimulated by radiation results not only in decreased IMS inside the $Si$-$SiO_2$ boundary but in decreasing the

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amount of defects in the intermediate layer, its ordering and improvement of MOS-structure electrophysical characteristics [83]. Bearing the above in mind, we used the method of photovoltage temperature dependences for studying the concentration and distribution of BES in the silicon forbidden gap in the $n$-Si(111)-$SiO_2$ structure in the course of its irradiation with nanosecond ruby laser pulses ($\lambda = 0.69$ μm) possessing the energy within the range $W = 0 - 1$ J/cm$^2$ [18]. The respective energy of quanta is sufficient only for being absorbed in silicon with creation of electron-hole pairs. The latter interact with Si and O atoms in the intermediate layer, which results in its structural changes, including changes in the BES system. Figs 5 and 6 show, respectively, the distributions of the BES concentration $N_{sf}$ in the silicon forbidden gap above $E_i$ and the maximum BES concentration $N_{sf}$ after exposure of the studied structure to light pulses with various energies $W$. It is seen that for pulse energies less than 0.6 J/cm$^2$ the BES concentration is decreased, which means that one can observe the light annealing of BES.

Only for laser pulse energies reaching or exceeding the silicon melting energy ($W \geq 0.7$ J/cm$^2$) one can observe an increase in the BES concentration. Fig. 5 also shows that in dependency on the energy of the irradiating pulse W the BES distribution in the forbidden gap changes. If before irradiation the $N_{sf\ \max}$ position corresponds to $E_i$+0.31 eV (which is in satisfactory accordance with the energy position of the $P_b$ center level [33] ), then after irradiation with increasing W the position of $N_{sf\,\max}$ shifts first to the c-band side and then to $E_i$.

Possibly, a change of the structure around $P_b$ center in the intermediate layer and/or the change of the broken

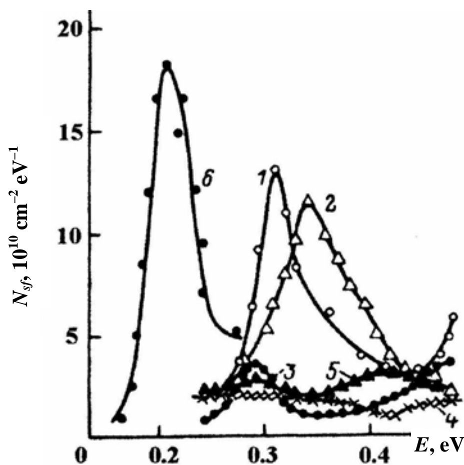


**Fig. 5.** Distribution of the BES density $N_{sf}$ at the Si surface *vs* the energy $E$ above $E_i$ after action of laser pulses: 1 – unirradiated thermally grown Si-$SiO_2$ system; 2 to 6 – irradiated with the laser pulses energies 0.1, 0.2, 0.3, 0.6, 0.7 J/cm$^2$, respectively.

orbital orientation are responsible for these phenomena.

Irradiation of Si-$SiO_2$ structures with ionizing radiation possessing high quantum energies (UV, X-ray, gamma-radiation) in most of the cases yields an increased BES and defect (traps for charge carrier) concentrations in $SiO_2$, if one does not perform the following annealing. In works [84, 85], developed was the model of arising in the $SiO_2$ near-boundary area E′ centers ($O_3\equiv$Si• defect) and non-bridging oxygen due to broken by radiation strained Si-O bonds. Displacments of the non-bridging oxygen defect (and H atom) in electric and IMS fields to the boundary results in uncoupled Si-Si bonds and creation of $P_b$ centers, *i.e.*, to the growth of the BES concentration. In [86], found was a good correlation between the E′ center concentration and the positive charge in oxide, between the $P_b$ center concentration and the BES density as well.

The structure Si-$SiO_2$ is unstable after radiation actions. ESR and spin-dependent recombination (SDR) investigations were carried out using MOS-structures with $n$- and $p$-channels (Si(100)-$SiO_2$ structure) after their irradiation with a proton beam possessing the mean energy 55 MeV or gamma-irradiation from the $^{60}$Co source [88]. It turned out that immediately after any kind of above irradiations one can find only $P_b$ centers and E′ defects. However, after hundred-hours aging the irradiated structures, there observed $P_{b1}$-centers arising as a result of defect-transformation processes. The $P_{b1}/P_{b0}$ center concentration ratio lay within the range 0–9 % in dependency on the time and conditions of aging. In particular, creation of $P_{b1}$ centers is enhanced by positive voltage (+3 V) applied to the gate of the MOS-transistor. In the course of aging, the concentration of $P_{b0}$ centers and E′ defects was not practically changed.

One interesting effect more was observed in the work [89]. The authors investigated the distribution of the BES concentration after UV and X-ray irradiations by using the method of measurements of charge pumping currents in MOS-elements with $n$- and $p$-channels and polysilicon gates used in serial integrated circuits. In original MOS-elements (before irradiation) after standard production of IC, they observed only small tails of the BES density near c- and v-bands, *i.e.*, levels caused by $P_b$ centers were absent. They did not appear after UV irradiation as well. If the MOS-elements are irradiated only with an X-ray beam ($5\cdot10^4$ R), wide peaks of the BES density appeared above and below $E_i$ in the range of $P_b$ center levels with maximum concentrations $N_{sf}$ = = $(2...3)\cdot10^{11}$ cm$^{-2}$eV$^{-1}$. However, consecutive irradiation of these MOS-elements with UV light and then with the same X-ray beam ($5\cdot10^4$ R) resulted in increasing the peak concentrations by more than the order of their magnitude ($> 3\cdot10^{12}$ cm$^{-2}$eV$^{-1}$). This effect of a “hidden” preliminary influence of UV irradiation the authors explained by the following mechanism. UV irradiation releases hydrogen atoms at the boundary polysilicon-$SiO_2$, which diffuse to the Si-$SiO_2$ boundary and in the course of the following X-ray

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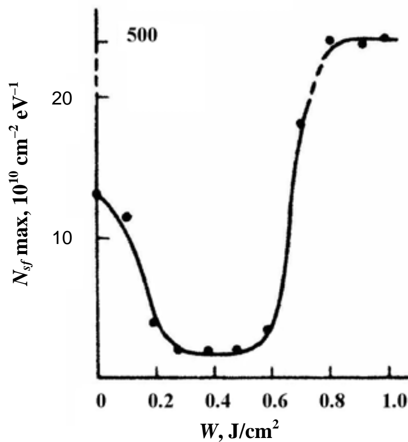


**Fig. 6.** Dependency of the peak Si BES concentration on the energy of laser pulses irradiating the Si-$SiO_2$ system.

irradiation take place in reactions resulting in $P_b$ center creation. Note that the thermal annealing (150 °C, 30 min) between UV and X-ray irradiations eliminated the influence of preliminary UV irradiation, while the annealing at 400 °C (20 min) absolutely eliminates the BES created both after the only X-ray and consecutive UV+X-ray irradiation.

### *6.3. Influence of strong electric fields on the BES system*

The BES system can be also transformed under the influence of electric fields applied to the MOS-structure in the course of its operation. Indeed, the $SiO_2$ film as well as intermediate layers of the Si-$SiO_2$ structure possess high internal electric fields, which results in creation of BES and defects in the $SiO_2$ film and, eventually, to full degradation of this film (its electric breakdown) [9-14]. The breakdown of a thick oxide layer ($d > 100$ nm) usually takes place in electric fields close to $8\cdot10^6$ V/cm, while considerable heating the charge carriers in their extended bands does at $(2...3)\cdot10^6$ V/cm. The breakdown field for a thin oxide layer ($d \sim 3...4$ nm) is approximately $(2...3)\cdot10^7$ V/cm as caused by destruction of Si-O bonds [90].

In the MOS-structure, when electric fields are sufficiently high but less than the breakdown ones, one can observe injection of charge carriers (electrons, holes) into $SiO_2$ both from silicon and the gate (consisting of metal or polysilicon). Being heated by electric field inside $SiO_2$, the injected carriers can create defects in $SiO_2$ and BES in silicon. In this case, there occur processes similar to those taking place in the MOS-structures under radiation exposure. In [91, 92], these processes were used to explain the BES density increase caused by avalanch injection of electrons and holes. It is worth to note an essential role of IMS being present both at the boundaries Si-$SiO_2$ and gate(metal)-$SiO_2$.

Rather interesting results were obtained in [93], these were different in the cases of electron or hole injection. Using the method of charge pumping, the authors determined the BES density distribution on (100) silicon surface in *p*-channel MOS-transistors with the thickness of $SiO_2$ subgate layer equal to 7 nm after various technological procedures. Directly after MOS-structure creation without annealing them in $H_2$, the BES distribution posseessed two broad peaks (above and below $E_i$) in the energy range of $P_{b0}$ and $P_{b1}$ centers. It is important to note that the method of charge pumping does not allow to separately determine levels created by $P_{b0}$ and $P_{b1}$ centers. Both peaks vanished after hydrogen passivation of these centers as a result of annealing them in $H_2$ atmosphere. The following injection of electrons into oxide, when the Fowler-Nordheim effect is valid, caused the predominant appearance of the BES above $E_i$, which means that the BES peak below $E_i$ was not practically created. To explain the fact, it was offered the so-called "hydrogenic" model of BES activation for the states located above $E_i$: H atoms (or ions) released by hot electrons move to silicon surface and create broken silicon bonds in accordance with the reaction: $\equiv$Si-H+$H^+$ +e $\rightarrow$ $\equiv$Si•+$H_2$. However, if one realizes hole injection from silicon into oxide, there arose the BES peaks approximately equal in their magnitude not only above but below $E_i$, too. In this case, it is assumed that the reaction $\equiv$Si-H+hole $\rightarrow$ $\equiv$Si•+H + hole is valid. The concentration of created BES increases with the level of hole injection but does not depend on the electric field strength in oxide $E_{ox}$ within the range $(1...5)\cdot10^6$ V/cm. The latter is in sharp contrast with the situation observed for electron injection, when increase in $E_{ox}$ from $2\cdot10^6$ up to $4\cdot10^6$ V/cm enhanced generation of BES located above $E_i$ by the order of value. This increase in the BES density with $E_{ox}$ is conditioned by an increase of the electron energy, which results in larger amount of released hydrogen for the former of above mentioned reactions to be realized on silicon surface. At the same time, holes even at $E_{ox} = 5\cdot10^6$ V/cm remain insufficiently energetic to enhance hydrogen release in oxide, as their mobility here is $10^6$ times lower than the electron one.

The authors of [93] conceive that the $\equiv$Si• defects obtained in reactions with hydrogen and hole participation differ, which results in doubled or single peaks in the silicon forbidden gap. It is not absolutely clear. Note in addition that another works demonstrated the fact that creation of the $\equiv$Si• defects due to splitting hydrogen from them in the course of high-temperature annealing lead to creation peaks both above and below $E_i$. Besides, known are the facts when at presence of the upper peak created by hot electrons or radiation the lower peak appeared after a long storage of the sample as a consequence of the intermediate layer structural transformation. In relation with it, remember that

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transformation of the intermediate layer caused creation of the $P_{b1}$ center, while immediately after radiation exposure only the $P_{b0}$ centers were present [88].
As the broad peaks of the BES density above and below $E_i$ include levels created by $P_{b1}$ and $P_{b0}$ centers, the way of BES creation due to electron or hole injection remains unclear. This is also complicated by the fact that separation of the hole and electron injection is very difficult sometimes, as it can take place simultaneously from the silicon substrate and from the gate of the MOS-system. It is noteworthy that hot holes are more efficient in BES generation than hot electrons at low levels of charge injection (below $10^{17}$ cm$^{-2}$), while the density of BES created by holes does not depend on the $SiO_2$ thickness but on the level of hole injection [94]. It is indicative of the fact that creation of BES by hot holes is the process inherent to Si boundary.

With a positive voltage on the MOS-structure gate possessing the thickness more that 4 nm, electron tunneling ensues from Si c-band into $SiO_2$ c-band through a triangular barrier (Fowler-Nordheim mechanism). However, when the $SiO_2$ thickness is about or lower than 3 nm, dominating is the direct tunneling of electrons from Si c-band into the gate by passing over $SiO_2$ c-band [14]. Besides, electron tunneling from BES into the gate is also possible [95]. These tunnel currents of electrons increase the total leakage current of the MOS-structures with thin $SiO_2$ layers and set the minimum possible for the $SiO_2$ thickness as 1.2 nm, which is sufficient to efficient operation of the MOS-devices. However, in [95] the real $SiO_2$ thickness in the efficiently operating MOS-structure was estimated as 3 nm. It is related with the considered in [95] recombination-tunnel mechanism of creating the BES by electrons, which results in the soft breakdown of $SiO_2$.

When the dielectric thickness is tunnel-transparent, it is also impossible to form an inversion layer on silicon surface by using external electric field, as the minority charge carriers are extracted from silicon into the gate. Note in summary that many questions of studying the MOS-structures with $SiO_2$ layers thinner than 4 nm have been considered in the review [14] where it is shown, in particular, that oxide degradation (breakdown of the MOS-structures) may be caused by creation of BES and traps in this oxide due to an applied electric voltage.

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