Charge Transport in Nonstoichiometric SiO$_x$ Obtained by Treatment of Thermal SiO$_2$ in Hydrogen Plasma of Electronic-Cyclotron Resonance

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Abstract—Currently, a new generation of high-speed, information-intensive resistive memory based on nonstoichiometric dielectrics is being developed. The electron structure of nonstoichiometric silicon oxide SiO$_x$ is set by the value of parameter $x$. It is found that the treatment of thermal SiO$_2$ in hydrogen plasma electron cyclotron resonance leads to the enrichment of silicon oxide with excess silicon, which in turn leads to the appearance of electron and hole traps in SiO$_x$. SiO$_x$ conductivity is bipolar: electrons are injected from negatively biased silicon and holes are injected from positively biased silicon. Cathodoluminescence (CL) experiments confirm the assumption that the traps in SiO$_x$ are due to the excess silicon.

$\textbf{p}^{++-}\text{Si}(100)/\text{SiO}_x/\text{Ni}$ memristor metal-dielectric-semiconductor (MDS) structures are fabricated based on the developed procedure for the preparation of nonstoichiometric oxide in hydrogen plasma of electron cyclotron resonance. Such structures have the properties of resistive switching of SiO$_x$ that do not require a forming operation.

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INTRODUCTION

Silicon oxide is a key dielectric in silicon devices. Thermal SiO$_2$ is used as a tunneling dielectric in modern flash memory devices [1]. The physical properties of nonstoichiometric silicon oxide SiO$_x$ are set by the parameter $x = [\text{O}]/[\text{Si}]$. The band gap of SiO$_2$ varies in the range from $E_g = 8.0$ eV in amorphous SiO$_2$ to $E_g = 1.6$ eV in amorphous Si [2–5]. Currently, resistive memory (resistive random-access memory, ReRAM) based on a reversible change in the conductivity of the dielectric layer under the action of electrical voltage pulses surpasses traditional flash memory in all key parameters: a large number of switching cycles $\sim 10^{10}$ [6, 7], low power consumption $<10$ fJ, and a high speed $\sim 0.3$ ns. The key element of the ReRAM cell is the metal dielectric metal (MDM). Various nonstoichiometric dielectrics such as HfO$_x$, TaO$_x$, TiO$_x$, SiO$_x$, GeO$_x$, AlO$_x$, NbO$_x$, SiN$_x$, and Si$_3$N$_4$ are studied as an active medium. The resistive switching properties of MDM structures appear after the so-called forming procedure, during which the MDM structure undergoes a soft electrical breakdown [8]. This operation is critical for the widespread adoption of ReRAM. The shaping operation consists of supplying a voltage pulse that, as a rule, is several times higher than the amplitude of the memristor switching pulses, which can lead to an irreversible dielectric breakdown or rapid degradation of the properties of resistive switching. It was previously shown that the forming operation can be avoided by lowering the forming voltage to values equal to the switching voltages of the memristor by using nonstoichiometric oxides of a certain composition obtained by ion beam sputtering deposition (IBSD) [9]. However, the IBSD method is not suitable for the ReRAM technology, since it does not allow obtaining conformal and uniform layers less than 10 nm thick. However, the thermal oxidation of Si ensures the conformity and homogeneity of SiO$_2$, but does not allow controlling the stoichiometry of the oxide layers. One of the ways to controllably introduce oxygen vacancies into oxide layers is through their treatment in hydrogen plasma of electron cyclotron resonance (ECR). This method was successfully tested by us in the reduction of SiO$_2$ to SiO$_x$ [4, 10] and V$_2$O$_5$ to VO$_2$ [11].
An important advantage of the electron cyclotron resonance plasma for the reduction process is the high degree of plasma ionization at a low ion temperature. It is known that the efficiency of ionization under conditions of electron cyclotron resonance is much higher than, for example, in planar HF plasma reactors. An HF ECR reactor allows a decrease in the plasma combustion pressure to $10^{-2}$–$10^{-3}$ Pa. During the treatment in ECR plasma, at a hydrogen pressure of less than $2 \times 10^{-2}$ Pa, the thermal effect on the surface of the film is insignificant, and it is possible to ensure that the temperature mode of the recovery remains unchanged throughout the entire process.

It is known that charge transport in thermal silicon oxide is limited by the Fowler–Nordheim tunneling injection [12]. The aim of this paper is to study the mechanism of charge transport in nonstoichiometric silicon oxide SiO$_x$ ($x < 2$) obtained by the reduction of thermal SiO$_2$ in hydrogen ECR plasma, as applied to the problem of creating a formless memristor based on SiO$_x$.

**FOUNDATIONS OF THE METHOD OF SEPARATING THE ELECTRON AND HOLE COMPONENTS OF THE CURRENT IN THE NONEQUILIBRIUM DEPLETION MODE OF SILICON**

In semiconductors, the sign of charge carriers (electrons and holes) is determined by measuring the Hall effect or thermo-EMF. Since the concentration of free charge carriers in dielectrics is negligible, the methods described above are inapplicable for them. In the general case, the conductivity of a dielectric is bipolar two-band, electrons are injected from a negatively biased contact (cathode), and holes are injected from a positively biased contact (anode) [13]. However, in dielectrics, the contribution of the electron and hole components to the injection current can vary greatly depending on the following factors: the height of the barrier at the contact-insulator interface, the pulse duration, the polarity of the potential, and the thickness of the dielectric [13]. To determine the contribution of electrons and holes to the conductivity of SiO$_x$ obtained by processing SiO$_2$ in hydrogen ECR plasma, in this study, we use the method of separating the electron and hole components of the current in the mode of nonequilibrium depletion of the metal–dielectric–semiconductor (MDS) on $n$- and $p$-type silicon, Figs. 1 and 2. This method using the example of Si$_3$N$_4$ was proposed and developed in [14–17]. Subsequently, this method was used to separate currents in HfO$_2$ [18], TiO$_2$ [19], and GeO$_2$ [20]. The method uses the external optical illumination to generate minority carriers and to determine their sign in the processes of injection from silicon into a dielectric.

Figures 1a and 1b show the energy diagram of the MDS structure based on $n$-Si/SiO$_x$/Ni and $p$-Si/SiO$_x$/Ni in the flat zone mode, without applied voltage. The values of electron and hole barriers at the Si/SiO$_x$ and Ni/SiO$_x$ interface and the band gap ($E_g = 7.3$ eV) of SiO$_x$ ($x = 1.96$) were determined using the data of quantum chemical calculations performed in [5].

Figures 1c and 1d show the energy diagram of the MDS structures based on $n$-Si and $p$-Si in the enrichment mode. In the silicon enrichment mode, practically all the applied voltage drops across the dielectric, since the potential drop across silicon is small. In this case, the space charge region is insensitive to the sign of the carriers in the dielectric.

In the silicon depletion mode, two options are possible. In the first case, when electrons or holes are injected from the metal into the dielectric, practically all of the applied voltage drops across the dielectric. The current in the MDS structure grows exponentially with an increase in the applied voltage. In the second case, when the minority carriers are injected from the semiconductor into the insulator due to the limited rate of thermal generation of the minority carriers, there is a decrease in capacitance, a transition of the capacitance from the inversion mode to the nonequilibrium depletion mode, and saturation of the through current. Backlighting increases the rate of generation of minority carriers in the space charge region of silicon, which leads to an increase in the saturation current. The saturation of the current in the nonequilibrium depletion mode indicates the injection of minority charge carriers from silicon into the dielectric.

Figures 1e and 1f show the energy diagram of the MDS structures based on $n$-Si and $p$-Si in the depletion mode in the case when the charge is transported by the minority carriers injected from silicon. The voltage drop in silicon leads to saturation of the minority carrier current from the semiconductor.

Independently, the sign of the charge carriers injected into a dielectric can be determined from the accumulation of charge carriers injected from silicon by measuring the shift of the capacity–voltage characteristics [20].

**EXPERIMENTAL**

SiO$_2$ layers were grown on $p$-$Si(100)$ 10 [$\Omega$ cm] and $n$-$Si(100)$ 4.5 [$\Omega$ cm] substrates with a diameter of 100 mm thickness 45 and 20 nm. After obtaining films of thermal SiO$_2$, the substrates were split into rectangular samples of $10 \times 18$ mm$^2$, which were exposed to hydrogen ECR plasma for 15 and 30 min.

The SiO$_2$ films were recovered in a vacuum unit assembled based on an evacuation station with a turbomolecular pump (residual pressure in the chamber $= 10^{-4}$ Pa), into which an antenna-type ECR plasma source with a multipole magnetic system was built, Fig. 2. The operating frequency of the source was 2.45 GHz. The ECR plasma was excited at a hydrogen pressure in a vacuum chamber of $1.8 \times 10^{-2}$ Pa, since
at this pressure the most stable plasma combustion was observed.

To carry out electrophysical studies, an Ni layer 50 nm thick was deposited on the samples after treatment by the method of electron beam evaporation through a metal mask. A schematic representation of structures for electrophysical measurements is shown in Fig. 3.

Additionally, we fabricated memristor MDS structures on degenerate silicon of the p-type with resistiv-

![Energy diagram of p-Si/SiO_x/Ni and n-Si/SiO_x/Ni structure in flat zone mode (a, b); in enrichment mode (c, d); and in the mode of nonequilibrium depletion (e, f). Curved arrow indicates media photogeneration under ambient lighting.](image)

**Fig. 1.** Energy diagram of p-Si/SiO_x/Ni and n-Si/SiO_x/Ni structure in flat zone mode (a, b); in enrichment mode (c, d); and in the mode of nonequilibrium depletion (e, f). Curved arrow indicates media photogeneration under ambient lighting.

![Schematic representation of a plasma ECR setup. View from above.](image)

**Fig. 2.** Schematic representation of a plasma ECR setup. View from above.
For an ellipsometric study of the effect of plasma ECR on the optical characteristics of SiO$_x$ films, we used two samples with a thermal oxide film thickness of 45 nm. One of the samples was treated in hydrogen plasma ECR for 15 min. The spectral dependences of the ellipsometric angles $\Psi(E)$ and $\Delta(E)$ were carried out using an Ellips-1891-SAG spectrophotometer (Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences (RISP SB RAS), Novosibirsk) under the following conditions: photon energy range $E = 1.13–4.96$ eV, spectral resolution of the device 0.01 eV, angle of incidence of the light beam on the sample 70°, and the recording time for one spectrum did not exceed ~20 s. A four-zone measurement technique was used with subsequent averaging over all zones. Measured spectra $\Psi(E)$ and $\Delta(E)$ were used further to solve the inverse problem of ellipsometry and determine the dispersion dependences $n(E)$ of SiO$_x$ films by fitting the calculated spectral dependences of the ellipsometric angles to the experimental ones in accordance with the single-layer optical model of the system [22]. The dispersion dependences were described using the Cauchy polynomial [23]:

$$n(E) = a + bE^2 + cE^4,$$

where $a$, $b$, and $c$ are coefficients. The optical constants $n$ and $k$ of the Si substrates for the calculations were taken from the database [24].

The SiO$_x$ film after treatment in ECR hydrogen plasma was simulated with a mixture of SiO$_2$ + SiO [25]. To assess the contribution of each component to the optical properties of the oxide, i.e., to estimate value $x$ in SiO$_x$, the Bruggeman effective medium model was used [26]:

$$\sum_i q_i \left( \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i + 2\varepsilon_{\text{eff}}} \right) = 0; \quad \sum_i q_i = 1,$$

where $q_i$ is the fraction of the $i$th component of the mixture; and $\varepsilon_i$ and $\varepsilon_{\text{eff}}$ are the dielectric constants for the $i$th component and effective environment.

To study the uniformity of thickness ($d$) and the refractive index ($n$) over the area of the samples of the initial films and after treatment in plasma, a Mikroskan-3M high-speed scanning high-resolution ellipsimeter (RISP SB RAS) was used [27]. The minimum step of shifting the ellipsometer stage along the $X$ and $Y$ axes was 5 μm, which determined the lateral resolution of the device. The ellipsometric angles were read over the surface area of 3 to 18 mm samples with a step along the $x$ and $y$ axes of 0.1 mm. We used a He-Ne laser ($E = 1.96$ eV), the angle of incidence of the light beam on the sample was 60°, the laser beam was focused into a 10 μm light spot on the sample surface using a high-quality nonpolarizing microlens. At each scanned sample point, the $d$ and $n$-film was calculated independently according to the method described above.
RESULTS AND DISCUSSION

Examination of the surface of the samples using a scanning ellipsometer showed that the film with thermal SiO₂ on the original sample has high homogeneity with the absence of gradients along \( d \) and \( n \) (Figs. 4a, 4b, 0 min). Treatment in hydrogen plasma did not lead to the appearance of experimentally noticeable absorption in the film. Therefore, in order to analyze the ellipsometric results, a single-layer model of a nonabsorbing film was also used.

Treatment in hydrogen plasma led to the appearance of inhomogeneities in \( n \) and \( d \): however, the values of these inhomogeneities did not exceed \( \Delta n \approx 1\% \) and \( \Delta d \approx 2\% \) (Figs. 4a, 4b, 15 min). In addition, the refractive index of the films increases insignificantly, and the film thickness remains practically unchanged (Table 1).

Figure 4c shows the spectral dependences \( n(E) \) of the samples under study obtained by processing the experimental spectra \( \Psi(E) \) and \( \Delta(E) \). It is seen that the treatment of SiO₂ in hydrogen plasma leads to a shift in the spectrum \( n(E) \) to the region of higher values of the refractive index. After 15 min of processing, the spectrum shift \( n(E) \) was \( \approx 0.01 \). The increase in the refractive index of the film, as shown by the CL method (see below), is determined by the process of partial reduction of the oxide with the formation of nonstoichiometric SiO\(_x\) [3].

To estimate parameter \( x \) in SiO\(_x\) from the optical measurements, the Bruggeman effective medium model was applied (2). It is assumed that nonstoichiometric SiO\(_x\) is formed in the form of silicon monoxide SiO. The best fit with the experimental curves was achieved (red dotted line, see Fig. 4c) in the case when the fraction of SiO in the layer was \( \approx 0.024 \), which made it possible to estimate the value of \( x \), which turned out to be \( \approx 1.96 \).

Figure 5 shows the experimental \( I–V \) characteristics of the \( p\)-Si/SiO\(_x\)/Ni structure measured at different temperatures and different potential polarities on Ni. Nonstoichiometric oxide SiO\(_x\) was obtained by 15 min of processing SiO\(_2\) films in hydrogen ECR plasma. To approximate the experimental results, we used the model of phonon-assisted electron tunneling between traps (Nasyrov–Gritsenko model) [28, 29].

The idea behind this model is that an electron in a trap goes into an excited state and tunnels into a neighboring trap when phonons are absorbed. It was found that the model of phonon-assisted tunneling between neighboring traps consistently describes the transfer of electrons in Ta\(_2\)O\(_5\) [30], SiO\(_2\) [31], HfO\(_2\) [32], Hf\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) [33], Si\(_3\)N\(_4\) [34], and Sc\(_2\)O\(_3\) [35].

Table 1. Results of ellipsometric measurements of samples before and after treatment in hydrogen plasma

| Plasma treatment time, min | Ellipsometric data |
|---------------------------|--------------------|
|                           | \( d, \text{ nm} \) | \( n, (E = 1.96 \text{ eV}) \) | parameters of the Cauchy model |
|                           | \( a \) \( \times 10^{-3} \) | \( b \) \( \times 10^{-4} \) | \( c \) \( \times 10^{-4} \) |
| 0                         | 40.3               | 1.462               | 1.447 | 3.970 | –0.166 |
| 15                        | 40.4               | 1.473               | 1.457 | 4.138 | –0.162 |
The expression for the probability of a phonon of facilitated tunneling and for the current density has form (3), (4):

$$P = \frac{2\sqrt{\pi} \hbar W_t}{m^* s^2 \sqrt{2kT (W_{\text{opt}} - W_t)}} \times e^{-\frac{W_{\text{opt}} - W_t}{kT}} e^{-\frac{qF}{\hbar}} \sinh \left( \frac{qFs}{2kT} \right),$$ (3)

$$J_{NG}(F) = P(F)qN_t^{3/2},$$ (4)

Here $q$ is the electron charge, $m^*$ is the effective mass of an electron, $\hbar = 2\pi \hbar$ is the Planck constant, $k$ is the Boltzmann constant, $N_t$ is the concentration of traps, $s = N_t^{-1/2}$ is the average distance between traps, $W_t$ is the thermal ionization energy of the trap, $W_{\text{opt}}$ is the optical energy of ionization of the trap, and $F$ is the electric field. As can be seen in Fig. 5, the phonon-assisted tunneling model clearly describes the experimental results for the following model parameters:

$m^* = 2.47m_0$, $W_t = 1.6$ eV, $W_{\text{opt}} = 3.2$ eV, and $N_t = 2.92 \times 10^{20}$ cm$^{-3}$ for a sample with a processing time of 15 min and a hole trap. For an electron trap, on the same sample, similar model parameters were obtained:

$m^*_e = 1.95m_0$, $W_t = 1.6$ eV, $W_{\text{opt}} = 3.2$ eV, and $N_t = 2.92 \times 10^{20}$ cm$^{-3}$, Fig. 5. The parameters of hole traps were obtained from the calculated curves describing the experimental $I$–$V$ characteristics measured at a negative potential on Ni (enrichment mode), and the parameters for electron traps were obtained from the calculated curves describing the $I$–$V$ characteristics at a positive potential on the Ni contact (depletion mode). Conductivity of the $p$-Si/SiO$_x$/Ni structure at a negative potential on Ni is determined by the holes injected from silicon, and at a positive potential, by the electrons also injected from Si, see Figs. 1c and 1e. It should be noted that the value of the current density in the enrichment mode of the $p$-Si/SiO$_x$/Ni structure shown in Fig. 5 is lower than that in the nonequilibrium depletion mode only for the reason that the measurement of the $I$–$V$ characteristics at different temperatures in the enrichment mode leads to a sharp increase in the current to values of $\sim 10$–100 mA and an irreversible breakdown of the structures at $E > 8$ MV/cm. Based on the results obtained, it can be concluded that during processing under the influence of hydrogen ECR plasma, structural defects, presumably oxygen vacancies, are introduced into the SiO$_2$ film. Moreover, the traps can capture both electrons and holes; i.e., they are amphoteric. Previously, the magnitude of the thermal $W_t = 1.6$ eV and optical $W_{\text{opt}} = 3.2$ eV of the traps’ energies for oxygen vacancies in SiO$_2$ were identified in [31]. The results of this study indicate that the values of the thermal and optical energy of the traps in SiO$_x$ are also $W_t = 1.6$ eV and $W_{\text{opt}} = 3.2$ eV.

The $C$–$V$ characteristics of the $p$-Si/SiO$_2$/Ni and $n$-Si/SiO$_2$/Ni structures for the initial sample with a layer of thermal SiO$_2$ that has not been treated in plasma are presented in Figs. 6a and 6b. In these structures, there is practically no hysteresis, which indicates the absence of electron and hole traps in thermal SiO$_2$.

Plasma treatment for 15 min leads to the accumulation of electrons and holes in the dielectric (Figs. 6c, 6d). The amount of accumulated charge increases as the plasma treatment time increases (Figs. 6e, 6f); treatment in this case was carried out for 30 minutes. At high depletion voltages, the capacitance transitions

![Fig. 5. Experimental $I$–$V$ characteristics of $p$-Si/SiO$_x$/Ni structures measured at different temperatures and different polarities of the potential on Ni and calculated curves obtained from the Nasyrov–Gritsenko model. Points, experimental data; lines, calculated curves.](image-url)
from the inversion mode to the nonequilibrium depletion mode. This phenomenon indicates the injection of minority carriers and electrons from silicon into the dielectric. The hysteresis of the $C–V$ characteristics indicates the injection and subsequent capture of electrons and holes; i.e., the conductivity of SiO$_x$ is two-zone.

Figures 7a and 7b show the $I–V$ characteristics of the $p$-Si/SiO$_2$/Ni and $n$-Si/SiO$_2$/Ni structures for samples with a layer of thermal SiO$_2$. In the enrichment mode, the current for both samples does not depend on illumination by an external source of optical radiation and grows exponentially with increasing voltage. On the $I–V$ characteristics of the $p$-Si/SiO$_2$/Ni sample in the depletion mode, with a positive potential on the metal, saturation of the current is observed, the level of which increases when the backlight is
turned on. As is known from [14], charge transport in SiO$_2$ is limited by the Fowler–Nordheim tunneling injection of charge carriers from silicon into the dielectric:

$$j_{FN} = \frac{\hbar q}{4\pi\epsilon_0 m^* F} F^2 e^{\frac{3\sqrt{2m^*qF\phi}}{\hbar}}. \quad (5)$$

Here $q$ is the electron charge, $m_0$ is the electron mass, $m^*$ is the effective mass of an electron, $\Phi$ is the height of the barrier for electron injection, $h$ is Planck’s constant, and $F$ is the electric field. The tunneling effective mass of electrons and holes in SiO$_2$ is $m^*_e \approx m^*_h \approx 0.5m_e$ [36, 38].

With a positive potential on silicon, the $I$–$V$ characteristics of the p–Si/SiO$_x$/Ni and n–Si/SiO$_x$/Ni structures are quantitatively described by the injection of holes from silicon. This circumstance is due to the fact that the barrier for electrons at the Ni–SiO$_x$ interface (4.04 eV) is greater than the barrier for holes at the Si–SiO$_2$ interface (3.6 eV) (Figs. 1c and 1f).

Figures 7c–7f show the $I$–$V$ characteristics of the p–Si/SiO$_x$/Ni and n–Si/SiO$_x$/Ni structures for samples treated in hydrogen plasma at different processing times. As described above, charge transport in such samples is described by the Nasyrov–Gritsenko model, Fig. 5.

In the depletion mode, the current is independent of the backlight and rises exponentially with increasing voltage. In the depletion mode, current saturation is observed, the level of which increases when the backlight is turned on. Consequently, according to the charge transport data, the conductivity of SiO$_2$ treated in the plasma is bipolar. Electrons are injected from a negatively biased electrode (silicon) and holes are injected from a positively biased electrode.

The injection of holes from silicon into SiO$_2$ is explained by a decrease in the hole barrier at the Si/SiO$_2$ interface. The enrichment with silicon is accompanied by a decrease in the electron and hole barriers at the Si/SiO$_2$ interface. For $x = 1.96$, the hole barrier’s height is 3.6 eV, which is 0.2 eV less than the barrier for holes at the Si/SiO$_2$ interface [5].

The CL spectra of silicon oxide films were measured before and after plasma treatment (Fig. 8a). It is known that in the visible range there are three bands related to the luminescence of point defects in silicon oxide. The 1.9 eV band is a nonbridging oxygen atom [39] and the 2.2 eV band does not have an unambiguous interpretation: however, this occurs with an oxygen deficiency [40] and 2.7 eV is an oxygen–deficiency center (ODC) [41]. The literature mainly describes two ODC models: a neutral oxygen vacancy ODC (I) [42] and a bicoordinated silicon ODC (II), denoted as =Si: [42, 43].

Figure 8b shows the decomposition of the CL spectrum for the initial sample with SiO$_2$ film on the three components indicated above. The CL spectra for the samples treated in hydrogen ECR plasma were decomposed in a similar way. The variation in the amplitude of the Gaussian peaks is shown in Fig. 8c. The concentration of traps $N_t$ was previously calculated by approximation by the phonon-facilitated tunneling model of the temperature dependences of the $I$–$V$ characteristics of MDS structures with the corresponding different processing times with the SiO$_2$ layers of the dielectric. It can be seen that the intensity of the 2.7 eV band changes significantly, it reaches the maximum at a plasma treatment time of 6 min, and then a slight decrease in intensity is observed, which may be related to concentration quenching. The intensity of the 1.9 and 2.2 eV bands increases after treatment in plasma for 2 min and then does not change, taking into account the error in determining the intensity for these bands.

The CL spectra in the UV range are shown in Fig. 8d. In this range, there is a band with the maximum at 4.5 eV, related to the ODC [41]. As in the 2.7 eV band, an increase in intensity is observed up to 6 min of treatment, and then a decrease, which can also be related to concentration quenching. Thus, it can be argued that plasma treatment leads to an oxygen deficiency in the silicon dioxide film and an increase in the intensity of the bands related to the centers of oxygen deficiency.

Figures 9a and 9b show the $I$–$V$ characteristics of the MDS memristor structures p+-Si/SiO$_x$/Ni, with SiO$_x$ 20 nm thick, at which resistive switching is observed. The processing time of the functional layer (SiO$_x$) in hydrogen ECR plasma for 6 and 15 min, respectively. Curve 1 corresponds to the initial $I$–$V$ characteristics of the MDS structures; in the literature, this process is called “forming.” During molding, the structure changes from an initial state to a low resistance (LRS) state. By reapplying a voltage of the same magnitude, the structure maintains a low resistance state. To switch the state of the MDS structure to the state of high resistance (HRS), it is necessary to apply a voltage of reverse polarity (curve 2). Similarly, to switch back to the LRS state, a positive voltage must be applied (curve 3). Such switches are called bipolar. It is clearly seen that the voltage of the first switch-on is either the same or less than the voltage of the subsequent switch-on. Such resistive switches are called forming-free.

**CONCLUSIONS**

In the bulk of SiO$_2$ silicon, the concentration of electron and hole traps is insignificant. The electron and hole conductivity of thermal SiO$_2$ is described by the Fowler–Nordheim tunneling mechanism.

Thermal SiO$_2$ treatment in hydrogen plasma leads to the appearance of a hysteresis of the volt–capacitance characteristics, which indicates the presence of
electron and hole traps in SiO_x. After plasma treatment, the conductivity of SiO_x is bipolar, electrons are injected into the dielectric from the negatively biased contact and holes are injected into the dielectric from the positively biased contact. This result follows from the saturation of the I–V characteristics in the mode of nonequilibrium depletion on silicon n- and p-types. Measurement of the C–V and I–V characteristics of the p–Si/SiO_x/Ni and n–Si/SiO_x/Ni structures showed that treatment in hydrogen ECR plasma is accompanied by a significant increase in the concentration of point defects in the dielectric. Taking into account
Fig. 8. (a) CL spectra in the visible range of silicon oxide films at different times of plasma treatment; (b) CL spectrum of the initial sample (black line) with SiO₂ film, Gaussian curves (red lines), and their sum (blue line); (c) dependence of the intensity of the CR bands on the content of traps. (d) UV CL spectra of silica films at different times of plasma treatment; (e) dependence of the intensity of the 4.45 eV CL band on the trap content.
that hydrogen plasma reduces oxides, the point defects are probably oxygen vacancies. This result is confirmed by the fact that the conductivity in such structures is clearly described by the phonon-assisted tunneling model. It was obtained from the simulation results that the energies of electron and hole traps in SiO$_x$ are the same: $W_t = 1.6 \text{ eV}$, $W_{opt} = 3.2 \text{ eV}$, and the concentration of traps depends on the treatment time in the plasma.

According to the CL results, it can be argued that plasma treatment leads to a deficiency of oxygen in the SiO$_x$ film and an increase in the intensity of the bands related to the centers of the oxygen deficiency. Based on the developed procedure for processing SiO$_2$ for films in hydrogen ECR plasma, ReRAM structures are created that do not require a forming operation, which is of great practical importance.

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**CONFLICT OF INTEREST**

The authors declare that they have no conflict of interest.

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