

NONSTATIONARY TRANSPORT OF ELECTRONS AND HOLES IN THE DEPOLARIZED MODE  
OF MNOS DEVICES: AN EXPERIMENT AND NUMERICAL MODELING

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In experiments performed while investigating stationary conduction in metal-nitride-oxide-semiconductor (MNOS) devices in the nonequilibrium depletion mode [1, 2] and separating the electron and hole components of current in MNOS transistors [3], it was proved that the transport voltage at both polarities near the semiconductor insulator interface is created by carriers injected from the silicon. It was uniquely established in experiments on blocking the injection of holes from the silicon that at a negative voltage ( $V < 0$ ) on the metal (Al, Au) in MNOS devices having a tunneling-thin layer of  $\text{SiO}_2$ , that charge transport was caused by holes and that the injection of electrons from the silicon was negligible [4]. Thus, when  $V < 0$  conduction in an MNOS device is a monopolar hole current (Fig. 1b).

It was established through experiment [1, 3, 5] that conduction in MNOS devices does not depend on the polarity of the voltage applied to the metal. This can be explained by two models. For the monopolar, two-zone model (A) charge is transported by holes when  $V < 0$ , and by electrons when  $V > 0$  (Fig. 1a). Model A assumes that the parameters of the hole and electron traps in the  $\text{Si}_3\text{N}_4$  are identical.

Model B for hole conduction assumes that, just as in model A, charge is transported by holes injected from the silicon when  $V < 0$  (Fig. 1c), and when  $V > 0$ , transport in the body of the  $\text{Si}_3\text{N}_4$  is limited by the transport of holes injected from the metal (Fig. 1c). The electrons injected from the silicon in model B recombine with holes in the traps that are responsible for the memory effect [6, 7].

The relationship between the hole and electron traps parameters in the  $\text{Si}_3\text{N}_4$  can be ascertained using either model of stationary conduction. A method for determining electron trap energy was developed in [8] in the isothermal depolarization mode. However, the interpretation of positive charge scattering adopted in this work was ambiguous.

The purpose of this article is to study hole and electron transport in the body of the  $\text{Si}_3\text{N}_4$  in the isothermal depolarization mode, to determine the parameters of the hole and electron traps, to compare the experimental results with those obtained through numerical analysis, and to discuss a possible model for deep trapping centers.

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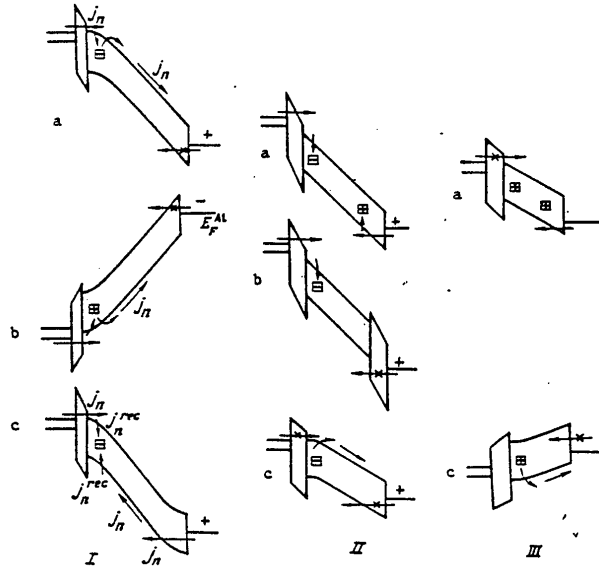


Fig. 1. Energy diagrams for MNOS devices: I) a tunnelling-thin oxide, stationary conduction; when  $V > 0$ : a), b) a monopolar, two-zone model A; b), c) hole conduction models B; b) monopolar conduction when  $V < 0$ ; c) bipolar conduction when  $V > 0$ . II) a tunnelling-thick oxide; a), b) nonstationary polarization mode for MNOS- (a) and MONOS- (b) devices; c) depolarization of MNOS devices - trapped electrons draining onto a metal electrode. III) accumulation (a) and depolarization (c) of holes.

**Specimens.** The parameters of deep trapping centers in silicon nitride depend on fabrication conditions. So that the results could be generalized, MNOS devices were studied in which the  $\text{Si}_3\text{N}_4$  was fabricated in low-pressure reactors by three different techniques. The  $\text{SiO}_2$  layers of thickness  $d_0 = 1.6-14$  nm were formed by thermally oxidizing silicon. Layers of aluminum and gold were used for the electrodes. A blocking layer of  $\text{Si}_3\text{N}_4$  was grown between the  $\text{SiO}_2$  and the metal in the metal-oxide-nitride-oxide-semiconductor (MONOS) devices.

**The Mathematical Model.** The one-dimensional model proposed in [9, 10]:

$$\frac{\partial n_s}{\partial t} + v_s \frac{\partial n_s}{\partial x} = -\sigma_s n_s v_s (N_t - n_t) + v' n_t \exp[-(\Phi_t - \beta F^{1/2})/kT] + I_s; \quad (1)$$

$$\frac{\partial n_t}{\partial t} = \sigma_t n_s v_s (N_t - n_t) - v' n_t \exp[-(\Phi_t - \beta F^{1/2})/kT]; \quad \frac{\partial^2 \Phi}{\partial x^2} = \frac{q}{\epsilon_N \epsilon_0} n_t; \quad \xi = \frac{4}{3\hbar} (2m^* q)^{1/2}, \quad (2)$$

$$I_s = j_{\infty} F_{\infty}^2 P_{\infty} P_N \Theta(x); \quad \Theta(x) = \frac{\exp(-\alpha(\Phi_0 - \Phi_t - \varphi(x)))}{\int_0^x \exp(-\alpha(\Phi_0 - \Phi_t - \varphi(x))) dx}; \quad (3)$$

$$P_{\infty} = \exp[-\xi(\Phi_0^* - (\Phi_0 - \varphi(0))^*)/F_{\infty}];$$

$$P_N = \exp[-\xi(\Phi_0 - \Phi_t - \varphi(0))^*/F(0)]$$

was used for analyzing the experimental data and studying the physical processes as the silicon nitride layers were polarized and depolarized. The initial and boundary conditions were chosen as

$$n_c(0, t) = I_0(0, t); \quad n_c(x, 0) = n_c(x, 0); \quad \varphi(0) = d_{ox} \frac{eN}{\epsilon_0} F(0); \quad \varphi(d_N) = V. \quad (4)$$

Here,  $n_c$ ,  $n_t$  are the concentrations of free and trapped electrons respectively;  $v_d$  is the drift velocity;  $\phi_t$  is the energy at the trapping center;  $\nu$  is a frequency factor;  $\phi_0 = 3.1$  eV;  $\phi_1 = 1.05$  eV is the height of the barriers at the Si-SiO<sub>2</sub> and SiO<sub>2</sub>-Si<sub>3</sub>N<sub>4</sub> interfaces respectively;  $I_0$  is the rate of carrier injection from the contact;  $V$  is the amplitude of the applied voltage;  $\alpha$  is the tunnel constant;  $d_{ox}$  and  $d_N$  are the oxide and silicon nitride layer thicknesses respectively, and  $j_{ox}$  is a constant that describes the current through the Si-SiO<sub>2</sub> contact.

The initial system of equations (1)-(3) were written as difference equations and Newton's iterative method, done by means of a matrix run, was used to solve them. The field and temperature dependence of the trapping section and the frequency factor were negligible in comparison with exponential factors.

#### ELECTRON TRANSPORT AND A COMPARISON OF THE EXPERIMENT WITH THE EXACT AND APPROXIMATE MODELS

The experiments were performed on MNOS devices having SiO<sub>2</sub> tunneling-impervious and tunneling-thick Si<sub>3</sub>N<sub>4</sub> ( $d_N > \bar{x} = \int_0^{d_N} xn, dx / \int_0^{d_N} n, dx$ ). Electrons were accumulated by applying a positive pulse to the Al-electrode (Fig. 1, IIa, b). The device was depolarized by an "attracting" positive voltage on the metal contact (Fig. 1, IIc). Parasitic effects may appear in this experiment and they must be considered: a) holes may be injected from the metal and accumulated near the Al-Si<sub>3</sub>N<sub>4</sub> interface during device polarization (Fig. 1, IIa, b) as electrons are scattered toward the metal electrode, the field at the Si-SiO<sub>2</sub> interface increases, increasing the probability that electrons will be injected from the silicon (Fig. 1, IIc).

As a rule, holes were seen to be injected from the metal when a positive voltage was applied to the aluminum in the polarizing mode. To reduce this injection a "natural" oxide was released from the Si<sub>3</sub>N<sub>4</sub> surface in a 10% solution of HF in water prior to depositing the aluminum. This treatment sharply curtailed the injection of holes. Holes injection was completely suppressed in the polarizing mode in MONOS devices because of the large barrier at the SiO<sub>2</sub>-Al interface (Fig. 1, IIb).

To block the injection of electrons from the silicon into the Si<sub>3</sub>N<sub>4</sub> in the depolarizing mode control experiments were arranged in which the critical value of the field at the Si-SiO<sub>2</sub> interface was experimentally determined at which the injection of electrons in the depolarizing mode was small.

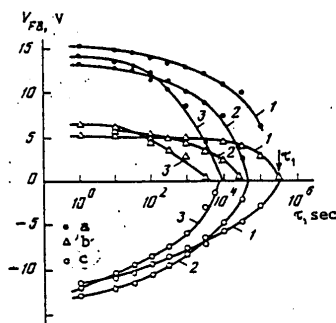


Fig. 2. Kinetics of depolarization for a), c) MNOS, and c) MONOS devices: a), b) electrons, c) holes;  $V$  (volts): 1) 30 V; 2) 40 V; 3) 50 V;  $T = 403^\circ\text{K}$ . MNOS)  $d_{ox} = 10$  nm,  $d_N = 180$  nm; MONOS)  $d_{ox}^I = 10$  nm,  $d_N = 175$  nm,  $d_{ox}^{II} = 5$  nm. Fabrication technique I (see Table 1).

TABLE 1. Parameters of Hole and Electron Traps in a Silicon Nitride Fabricated by Different Techniques (LPR = low press. reactor)

Fabrication parameters	Electron traps parameters	Hole traps parameters
I LPR, 750° C SiCl <sub>4</sub> :NH <sub>3</sub> = 1:10	$\Phi_e = 1.4 \pm 0.1$ eV $\nu^e = 3 \cdot 10^{21} \text{ sec}^{-1}$ $N_{it}^e = (2 \pm 1) \cdot 10^{18} \text{ cm}^{-3}$ $\sigma_e^e = (2 \pm 1) \cdot 10^{-13} \text{ cm}^2$	** $\Phi_h = 1.35 \pm 0.05$ eV $N_{it}^h = (3 \pm 1) \cdot 10^{18} \text{ cm}^{-3}$ $\sigma_h^h = 10^{-13} \text{ cm}^2$
II LPR, 900° C SiCl <sub>4</sub> :NH <sub>3</sub> = 1:20	$\Phi_e = 1.5 \pm 0.1$ eV * $\Phi_e = 1.45 \pm 0.05$ eV $\nu^e = 10^{21} \text{ sec}^{-1}$ $\nu^e = 10^{21} \text{ sec}^{-1}$ $N_{it}^e = 2 \cdot 10^{18} \text{ cm}^{-3}$ $\sigma_e^e = 3 \cdot 10^{-13} \text{ cm}^2$	$\Phi_h = 1.5 \pm 0.1$ eV $\nu^h = 10^{21}$ - -
III LPR, 850° C SiH <sub>4</sub> :NH <sub>3</sub> = 1:30	$\Phi_e = 1.4 \pm 0.1$ eV $\nu^e = 10^{21} \text{ sec}^{-1}$ $N_{it}^e = 4 \cdot 10^{18} \text{ cm}^{-3}$ $\sigma_e^e = 4 \cdot 10^{-13} \text{ cm}^2$	$\Phi_h = 1.4 \pm 0.1$ eV * $\Phi_h = 1.5 \pm 0.1$ eV $\nu^h = 10^{21} \text{ sec}^{-1}$ -

Comment. Values of  $\phi_e^e$ ,  $h$  and  $\nu^e$ ,  $h$  were determined by the discharge in MNOS devices having a thick SiO<sub>2</sub> layer according to the simplified model; \*  $\phi_e^e$  and  $\nu^e$ ,  $h$  were obtained by comparing the experiments on discharge with the exact model; and  $\tau_{\phi}^h$  were determined in an MNOS device having a thin SiO<sub>2</sub> layer in the stationary conduction mode.

The kinetics of negative charge scattering in an MNOS device (a specimen in which holes were seen to be strongly injected from Al) and a control MONOS device are shown in Fig. 2. Under identical polarizing conditions,  $V = +75$  V and  $\tau = 5$  sec, it is obvious that the initial negative charge stored in the MNOS device is substantially less than that in the MONOS device. This difference is caused by holes injected from the aluminum during polarization being trapped (Fig. 1, IIa).

An approximation

$$\tau \approx \nu^{-1} \exp \left[ \left( \Phi_e - \beta \bar{F}^h \right) / kT \right] \quad (5)$$

of the characteristic information storage time was used to analyze experimental data in [8], where  $\bar{F}$  is the characteristic field in which depolarizing is performed. A qualitative estimate of the applicability of Eq. (5) for analyzing experimental data was made via mathematical modeling.

A simple model based on Eq. (5) assumes that repeated trapping can be neglected in the Si<sub>3</sub>N<sub>4</sub>. This is in line with the smallness of the first term in the right-hand side of Eq. (1) in comparison with the second term.

The evolution of the distribution of populated traps when repeated trapping is and is not present is shown in Fig. 3a. When repeated trapping is not present, the traps are discharged from the strong field-metal electrode side. A region that was initially unoccupied by electrons remains unfilled throughout the entire scattering process.

In considering repeated trapping the maximum traps populating region is displaced toward the metal electrode (Fig. 3a) which produces a more uniform spatial distribution of the field (Fig. 3c). This effect is caused by a strong retrapping effect. The trapping and ionization rates differ insignificantly (see Fig. 3b) and, in spite of the fact that the ionization rate over long time spans is a maximum in the region near the anode because of strong trapping in this region, the region near the cathode makes the principal contribution to emptying the traps.

At first glance the data of Fig. 3 indicate that the simplified model used in [8] is inapplicable. A more detailed inspection, however, reveals that this is not the case. It can be seen from Fig. 3c that although the maximum difference in the field caused by the charge from local electrons is about 25%, and the difference between the local field and the anode field at the point of maximum ionization is about 10%. Thus, using Eq. (5) gives a relative error  $\delta = 2\Delta F / 2\phi_e^e \bar{F}^{1/2} \sim 1.5\%$  (for  $\bar{F} \sim 1 \cdot 10^6$  V/cm) in determining the energy of the level that is substantially less than the experimental error.

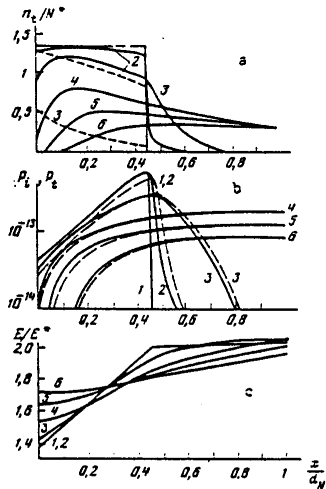


Fig. 3

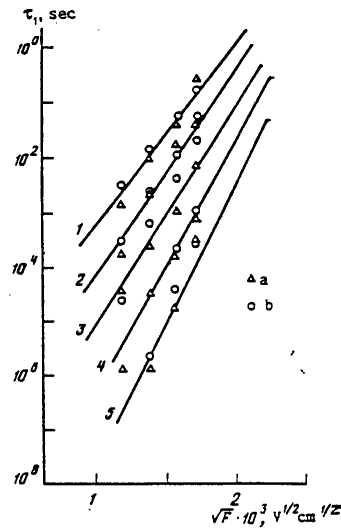


Fig. 4

Fig. 3. Spatial distribution of local electron concentrations (a), the electric field (c), and the trapping rate  $P_t$  (dashed line) and traps ionization  $P_i$  (solid line) (b) in the  $\text{Si}_3\text{N}_4$  at different moments in time as an arbitrarily stored charge is scattered;  $t$  (seconds)=: 1) 0; 2) 1.6; 3) 22; 4) 104; 5) 203; 6) 303.  $d_N = 180 \text{ nm}$ ,  $d_{ox} = 10 \text{ nm}$ ,  $N_t = 6 \cdot 10^{18} \text{ cm}^{-3}$ ,  $\phi_{te} = 1.4 \text{ eV}$ ,  $v^e = 10^8 \text{ sec}^{-1}$ ,  $\sigma_t = 4 \cdot 10^{-13} \text{ cm}^2$ ,  $N^* = 3 \cdot 10^{17} \text{ cm}^{-3}$ ,  $F_0 = 1.35 \cdot 10^6 \text{ V/cm}$ ,  $V = +50 \text{ V}$ ,  $T = 453 \text{ K}$ ,  $P_t = \sigma_t n_c v_d (N_t - n_c)$ ,  $P_i = v^e n_c \exp [(\phi_{te} - \beta F^{1/2})/kT]$ .

Fig. 4. Characteristic time  $\tau_1$  as a function of the electric field in silicon nitride at coordinates corresponding to the Frenkel effect of Eq. (5): (a) electrons, (b) holes;  $d_{ox} = 50 \text{ nm}$ ,  $d_N = 150 \text{ nm}$ . Fabrication technique) III. (1) 573°K, (2) 513°K, (3) 473°K, (4) 413°K, (5) 373°K.

The physical basis for using the simplified model is that the characteristic time  $\tau_1$  for thermally ionizing the traps is more than ten times greater than the characteristic trapping time  $\tau_t = (N_t \sigma_t v_d)^{-1} = 10^{-12} \text{ sec}$  (for  $N_t = 10^{18} \text{ cm}^{-3}$ ,  $\sigma_t = 10^{-13} \text{ cm}^2$  and  $v_d = 10^7 \text{ cm/sec}$ ) and the characteristic drift time is  $\tau_{dr} = d_N/v_d = 10^{-12} \text{ sec}$  so that traps ionization is the limiting factor and, on the whole, the kinetics of scattering are satisfactorily described by the Frenkel effect of Eq. (5). An analysis of the experimental data by the approximate model and by comparison with exact numerical computations shows that, within the limits of experimental error, the parameters  $\phi_{te}$  and  $v$  coincide.

Numerical modeling of the depolarization process showed that the kinetics of charge scattering significantly depends on the initial voltage bias of the plane zones  $\Delta V_{FB}$ , but depends only weakly on the combined effects of the magnitude of the charge and its centroid  $\bar{x}$ . In consideration of this fact, the characteristic discharge time  $\tau_1$  assumed a value obtained by extrapolating the dependence  $\Delta V_{FB}(\log \tau)$  to zero. It follows from Fig. 2 that values of  $\tau_1$  in an MNOS device, where the injection of holes during polarization is blocked, and in an MNOS device, where the injection of holes is substantial, are close. The function  $\tau_1 = f(F, T)$  for electrons is shown in Fig. 4 for a different  $\text{Si}_3\text{N}_4$  fabrication technique. Functions corresponding to Eq. (5) for  $\epsilon_{ox} = n^2 = 4$  are shown by lines in Fig. 4. An analysis of the experiment by the approximate model yields  $\phi_{te} = 1.37 \pm 0.1 \text{ eV}$ ,  $v^e = 10^8 \pm 1 \text{ sec}^{-1}$ . Devices having the silicon nitride obtained by the other fabrication techniques were studied in a similar fashion. The parameters for deep trapping centers in the nitride, obtained by different techniques, are shown in Table 1.

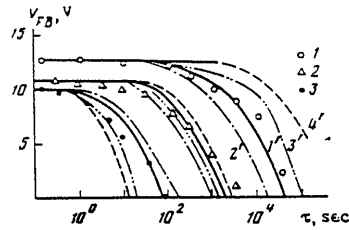


Fig. 5. Kinetics of electron scattering at different temperatures;  $V = +40$  V, experiment:  $T = (1) 403^\circ\text{K}$ ,  $(2) 453^\circ\text{K}$ ,  $(3) 523^\circ\text{K}$ . Computation of  $\phi_{\tau}^e$  and  $\nu^e$  respectively:  $(1')$  1.4 eV,  $2 \cdot 10^8 \text{ sec}^{-1}$ ;  $(2')$  1.35 eV,  $5 \cdot 10^7 \text{ sec}^{-1}$ ;  $(3')$  1.5 eV,  $2 \cdot 10^9 \text{ sec}^{-1}$ ;  $(4')$  1.6 eV,  $2 \cdot 10^{10} \text{ sec}^{-1}$ . Device parameters are the same as in Fig. 2.

numerical analysis showed that varying the electric field  $F$  (when  $T = \text{const}$ ) allows to be determined, but does not offer the opportunity of uniquely determining  $\phi_{\tau}$  and  $\nu$ . It is possible to uniquely determine the magnitudes of the frequency factor and the level by comparing the results of the computations and the experiments performed at different temperatures with a constant electric field intensity. Varying  $\nu$  shifts the kinetic function along the  $\lg \tau$  axis and the value of  $\phi_{\tau}$  affects the value of the characteristic spacing (its of  $\lg \tau_1$ ) of curves taken at different temperatures. This analysis for the data of yields  $\phi_{\tau}^e = 1.45 \pm 0.05$  eV and  $\nu^e = 10^8 \pm 1 \text{ sec}^{-1}$ . Processing these experiments by the approximate model yielded  $\phi_{\tau}^e = 1.5 \pm 0.1$  eV and  $\nu^e = 10^7 \pm 1 \text{ sec}^{-1}$ . The parameter values derived by the exact and the approximate models are in good agreement.

#### NONSTATIONARY HOLES TRANSPORT

In MNOS device having a gold electrode was used to store a positive charge. Storing the from silicon in devices having a thick  $\text{SiO}_2$  layer is difficult because of the large potential barrier at the  $\text{Si-SiO}_2$  interface and holes are therefore stored in MNOS devices by injecting a charge from the positively biased gold electrode (Fig. 1, IIIa) at a temperature  $30^\circ\text{K}$ . It was established that carrier injection in this case was caused by a thermally assisted tunneling mechanism [3]. To explain the affect of the contribution made by the positive injection of electrons from the silicon during polarization, the bias voltage in the  $r$  zones  $\Delta V_{FB}$  was compared with the charge in the external circuit. The following equation

$$\Delta V_{FB} \approx \int j_{\text{ext}}(t) dt. \quad (6)$$

is found to be accurate to within 10%, where  $j_{\text{ext}}$  is the current in the external circuit. Equation (6) is satisfied when the amount of electrons injected from the silicon is small. In addition, direct support for blocking of electron injection from the silicon into the  $\text{Si}_3\text{N}_4$  at charge storage in the control MNOS devices having an aluminum electrode is absent.

Following polarization, a negative voltage was applied to the metal electrode and the kinetics of the holes draining onto the metal electrode at different field tensions and temperatures was studied (Fig. 1, IIIc).

An analysis similar to that made for stored charge scattering was made of the kinetics of depolarizing positively charged MNOS devices (Fig. 2). In keeping with the experimental (Figs. 2, 4) the kinetics of hole and electron transport agree within the limits of error for a given  $\text{Si}_3\text{N}_4$  fabrication technique, i.e.,

$$\phi_{\tau}^e = \phi_{\tau}^h, \quad \nu^e = \nu^h. \quad (7)$$

satisfied.

#### THE MODEL FOR DEEP CENTERS

We will isolate the basic properties of trapping centers: a) the symmetry of the hole and electron traps parameters: the relations  $\phi_{\tau}^e = \phi_{\tau}^h$ ,  $\nu^e = \nu^h$ ; b) activation energy as

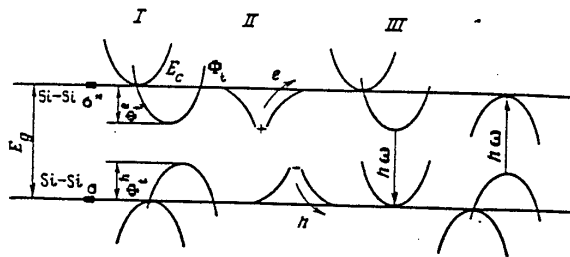


Fig. 6. A polaron model for carrier trapping in  $\text{Si}_3\text{N}_4$  at a neutral  $\equiv\text{Si-Si}\equiv$  defect. The configuration diagrams illustrate multiphonon trapping and the recombination of local carriers with free carriers of opposite sign: I) multiphonon capture; II) emission; III) trapping and recombination;  $E_g = 4.6$  eV.

functions of electric field intensity (the Frenkel-Poole effect) and the large trapping  $\sigma_c^e = \sigma_c^h = 5 \cdot 10^{-13}$   $\text{cm}^2$  [12] attest to the far-reaching nature of the voltage (at distances,  $\sim 1$  nm, the voltage is near a Coulomb voltage), and; c) the large recombinations for holes and electrons that were observed experimentally in the  $\text{Si}_3\text{N}_4$ :  $\sigma_r = 3$   $\text{cm}^2$  in [7] and  $\sigma_r = 5 \cdot 10^{-14}$   $\text{cm}^2$  in [13].

The model for a compensated semiconductor [3], in particular the volt-ampere characteristics of the defects [14], may explain the first two properties, however, they do not explain the large recombination sections.

It is possible that the properties observed can be explained by a polaron model on the hypothesis that neutral  $\text{Si}_3\text{N}_4$  defects exist in the  $\equiv\text{Si-Si}\equiv$  [15, 16]. The bonding and antibonding  $\sigma^*$ - orbitals in such a defect coincide with the edges of the  $E_v$  and  $E_c$  in (Fig. 6). Localizing holes and electrons proceeds via multiphonon transition into a state having negative energy  $\phi_c^*$ . The gain in energy due to polarizing the lattice during trapping on a defect of radius  $R_0$  can be estimated by Mott's formula:

$$\Phi_c \approx -q^2/\epsilon_p R_0; \quad \epsilon_p^{-1} = \epsilon_\infty^{-1} - \epsilon^{-1}.$$

In  $\text{Si}_3\text{N}_4$ ,  $\epsilon_\infty = 4$ ,  $\epsilon = 7$ , and the value  $\phi_c \approx 1.5$  eV corresponds to  $R_0 = 0.1$  nm. The trapping section in this model is qualitatively explained by the fact that the wave functions of the  $\sigma$ - and  $\sigma^*$ - orbitals are very delocalized. The large recombination section is explained by Coulomb attraction of local carriers to free carriers having opposite sign. Parameters that depend on the sign of the charge carrier (e.g.,  $m^*$ ) do not appear in Eq. (8), the polaron model explains the equality  $\phi_c^e = \phi_c^h$ . The  $\equiv\text{Si-Si}\equiv$  defects model explains the absence of diamagnetic centers in unpolarized  $\text{Si}_3\text{N}_4$  [15]. Equation (8) is inwardly contradictory, because the macroscopic parameter  $\epsilon_p$  appears along with the microscopic parameter  $R_0$  at characteristic dimensions of which the  $\epsilon$  concept in the problem loses strict meaning. Also, the individual properties of the defect at which the polaron was trapped do not appear in Eq. (8).

#### DISCUSSION OF RESULTS

The principal result of this work is experimental proof that the parameters of hole and electron traps in the body of the  $\text{Si}_3\text{N}_4$  are equal. From this fact and the injective nature of conduction in the  $\text{Si}_3\text{N}_4$  [18] we can draw the general conclusion that the sign of the charge carrier in the  $\text{Si}_3\text{N}_4$  is determined by the barrier, which assures a high level of carrier injection for a given polarity.

The potential barrier for electrons at the Al- $\text{Si}_3\text{N}_4$  interface is  $\phi_{0e} = 2.0-2.1$  eV and the corresponding barrier for holes lies in the  $\phi_{0h} = 2.5-3.0$  eV range [19]. Even when a positive voltage is applied to the metal (Al) in MNOS devices having a thin  $\text{SiO}_2$  layer, hole injection from the Al into the  $\text{Si}_3\text{N}_4$  is negligible in comparison with holes injection from silicon [4]. From here it follows that holes injection from the Al into the  $\text{Si}_3\text{N}_4$  is less likely at a positive voltage in comparison with electrons injection at another voltage (because  $\phi_{0h} > \phi_{0e}$ ). Thus, from the barrier parameters at the contacts point of view we can conclude that when a positive voltage is applied to the metal, electrons are the main

contributors to conduction in MNOS devices. In other words, an MNOS device having an aluminum electrode is well described by model A. However, the possibility of realizing model B is not excluded. This variant of conduction apparently occurs in devices having gold or partially silicon electrodes (when  $V > 0$ ) or with a negative bias on the metals with little work at the output. Bipolar injection was observed experimentally in a nonstationary mode in [20] and was analyzed theoretically in [6, 21].

The results of this work do not clarify the nature of the unusually small value of the frequency factor  $\nu$ . Note that values of  $\nu = 1.2 \cdot 10^8 \text{ sec}^{-1}$  were observed in [22] and  $\nu = 5 \times 10^8 \text{ sec}^{-1}$  in [23].

#### CONCLUSIONS

1. A method of determining the parameters  $\phi_c$  and  $\nu$  for hole trapping centers was proposed and realized experimentally.
2. It was experimentally established that the parameters of deep electron and holes centers are

$$\phi_c = \phi_c^*, \quad \nu = \nu^*$$

for all three  $\text{Si}_3\text{N}_4$  fabrication techniques.

3. A numerical analysis of the kinetics of depolarizing a negative charge was made. Charge scattering is accompanied by intense retrapping. Nevertheless, the experiment is satisfactorily described by the simplified model, not considered trapping.

4. A polaron model of holes and electrons trapping on a neutral  $\equiv\text{Si}-\text{Si}\equiv$  defect in  $\text{Si}_3\text{N}_4$  was proposed. In keeping with this model, electrons (holes) were initially trapped in the antibonding (bonding) orbitals of an Si-Si defect that coincide with the  $E_c$  and  $E_v$  zone edges in the  $\text{Si}_3\text{N}_4$ . Carriers were localized by the subsequent multiphonon transition. The model explains the basic experimental data for the transport of holes and electrons in  $\text{Si}_3\text{N}_4$  qualitatively.

5. The equality of the parameters for deep centers and the relationship of potential barriers for injecting holes and electrons in MNOS devices support using the two-zone monopolar model to describe conduction in the  $\text{Si}_3\text{N}_4$ , i.e., by electrons when a positive voltage is applied to the aluminum and by holes when a negative voltage is applied - not by the hole model proposed in [6, 7].

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## FRENKEL-LIMITED MONOPOLAR CONDUCTIVITY OF MNOS STRUCTURES

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The reduction in the thickness of  $\text{Si}_3\text{N}_4$  films associated with increasing integration of MNOS memory matrices has stimulated research on the physical mechanisms of charge transfer in dielectrics. There is no unique interpretation of the experimental data. In particular, two models are used to explain the conductivity of MNOS structures:

1. The monopolar two-band model [1, 2], according to which for both polarities of the potential  $V_g$  applied to a metallic contact (Al) charge transfer is realized by carriers injected from the silicon.
2. The hole model, according to which for  $V_g < 0$  transfer is realized by holes injected from the silicon, while for  $V_g > 0$  it is realized by holes injected from the Al electrode [3, 4].

The numerous experiments on stationary currents in the state of nonequilibrium depletion or MNOS structures [1, 5] and on the separation of the electronic and hole components of the current in MNOS transistors [2, 4, 6] do not permit choosing unequivocally one or the other model.

The first theoretical studies of the transition from the nonstationary to the stationary state, carried out in [7] and independently in [8], demonstrated the determining effect of space charge on current flow in both states. However, a number of questions have remained unresolved.

The purpose of this work is a) to clarify the limiting factors of charge-carrier transfer in the nonstationary and stationary states under conditions of polarization of the structure and b) to make a quantitative comparison of the experimental results on the conductivity of MNOS structures with  $\text{Si}_3\text{N}_4$  layers of different thickness over a wide range of fields and temperatures with numerical calculations based on the monopolar, one-level model.

## EXPERIMENT

The experimental data were obtained on MNOS structures with an  $\text{SiO}_2$  film thin enough (20 Å) to permit tunneling. The thickness of the  $\text{Si}_3\text{N}_4$  layer in different structures equaled  $d_N = 390, 740, 1350, \text{ and } 2500$  Å. The silicon nitride layers were obtained from  $\text{SiH}_4$  and  $\text{NH}_3$  in a low-pressure reactor,  $T_{\text{syn}} = 850^\circ\text{C}$ , and  $\text{SiH}_4/\text{NH}_3 = 1:30$ . The metallic contact consisted of an Al electrode with an area of  $S = 5 \cdot 10^{-3}$  cm<sup>2</sup>. Silicon nitride prepared in this manner is characterized by the existence of trapping centers with energy  $\approx 1.4$  eV, which is convenient for the experimental study of the conductivity because of the insignificant relaxation of the current when a constant voltage is applied. Since the main evolution is over  $\approx 1$  sec after the external voltage is applied, after which long-time current relaxation with an insignificant change in the magnitude of the current ( $\approx 10\%$ ) occurs, the current measured 3 min after the onset of polarization was adopted arbitrarily as the quasistationary value of the current.

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