Journal of Applied Physics

RESEARCH ARTICLE | JULY 03 2024

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J. Appl. Phys. 136, 014101 (2024)
https://doi.org/10.1063/5.0215684

Journal of Applied Physics | ARTICLE | pubs.aip.org/aip/jap

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Cite as: J. Appl. Phys. **136**, 014101 (2024); doi: 10.1063/5.0215684
Submitted: 25 April 2024 · Accepted: 16 June 2024 ·
Published Online: 3 July 2024

View Online Export Citation CrossMark

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ABSTRACT

The spectrum of localized hole states (traps) in amorphous silicon nitride, a-Si_3N_4, is experimentally studied using the method of thermally stimulated depolarization. The experiment is compared with theoretical calculations using three models of the energy spectrum of traps: discrete spectrum (monoenergetic trap), continuous spectrum, and Gaussian trap distribution. The experiment is quantitatively described by a model of a discrete spectrum of traps with an energy of 1.15 eV and a width of no more than 0.01 eV. In the case of a continuous and Gaussian spectrum of traps, the contribution to depolarization is made by the deepest traps. The blurring of the trap energy level in a-Si_3N_4 due to the absence of long-range order (fluctuations in the Si–N bond length and fluctuations in the N–Si–N and Si–N–Si angles) does not exceed 0.01 eV.

I. INTRODUCTION

The fundamental difference between an amorphous solid and a crystalline one is the absence of long-range order in the arrangement of atoms. The absence of long-range order leads to the blurring of edges of the valence band and conduction band.[1,2] Amorphous semiconductors and dielectrics are characterized by the presence of localized states.[1,2] A typical dielectric with a high (10^{18}–10^{21} cm^{-3}) concentration of localized states (traps) is amorphous silicon nitride (a-Si_3N_4).[3] Due to the presence of traps, a-Si_3N_4 has a memory effect, the ability to localize electrons and holes injected into it with a gigantic (10 years at 85 °C) lifetime of electrons and holes in a localized state. The memory effect underlies the physical principle of modern flash memory operation—Charge Trap Flash TaN/Al_2O_3/Si_3N_4/SiO_2/Si (TANOS),[4,5] which retains information when the power is turned off, is shown in Fig. 1.

In the programming mode, when a voltage pulse is applied to the gate, electrons or holes (depending on the potential polarity) tunnel through SiO_2 into the storage medium of a-Si_3N_4 containing deep electron and hole traps. The blocking high-k dielectric prevents a parasitic injection of electrons and holes from the gate into the a-Si_3N_4 memory.[6] Electrons or holes accumulated in a-Si_3N_4 lead to the formation or absence of a conducting channel between the source and drain in a TANOS transistor. In this way, the TANOS transistor stores one bit of information without consuming energy. Currently, a-Si_3N_4 is a model material for studying the processes of localization/delocalization and transport of electrons and holes in dielectrics.[3]

In doped semiconductors, donors and acceptors produce discrete levels in the bandgap.[7,8] It is assumed that, in amorphous semiconductors and dielectrics, potential fluctuations caused by the absence of long-range order lead to the energy broadening of discrete levels.[1,2]

Currently, ideas about the energy spectrum of localized states in a-Si_3N_4 are contradictory.[9–21] These ideas can be roughly divided into two categories (Fig. 2). Experiments on the charge transport in a-Si_3N_4 are interpreted on the basis of the concept of discrete monoenergetic electron and hole traps (positions a–c in Fig. 2).[9–11] Quantum chemical modeling also predicts the presence of discrete levels in a-Si_3N_4.[12–16] Experiments on the depolarization of a-Si_3N_4 are interpreted based on the idea of a continuous spectrum of electron and hole traps. The conceptions of traps continuum, in turn, fall into two categories. Some experiments predict the presence of a broadened level of traps (positions d–f in Fig. 2, width up to 1 eV).[17–19] Other experiments predict the presence of a continuous spectrum of traps with a width of about 1 eV cm at the g–h position in Fig. 2.[20,21] Thus, there is a fundamental contradiction

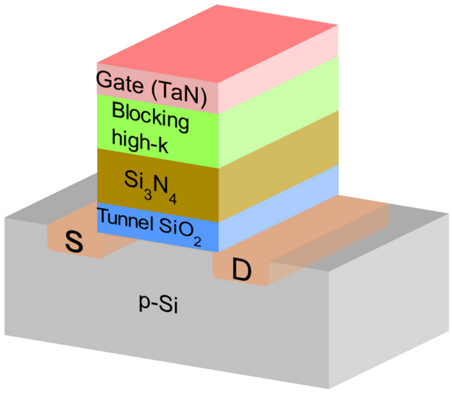

FIG. 1. Structure of a modern charge trap flash memory element.

about the energy spectrum of electron and hole traps in a-Si_3N_4. Resolving this contradiction is important both from a fundamental point of view about the nature of the energy spectrum of localized states in amorphous dielectrics and from the point of view of understanding and modeling the processes of electron and hole retention in flash memory elements based on the charge localization in a-Si_3N_4. The thermally stimulated depolarization (TSD) method is an effective method for the spectroscopy of localized states in semiconductors and dielectrics.[22–24]

The aim of this work is to establish the energy spectrum of hole traps in a-Si_3N_4 using TSD experiments, and a spectrum analysis based on the theory of trap multiphonon ionization.

II. EXPERIMENTAL AND CALCULATION METHODS

Metal (Al)–nitride (40 nm)–SiO_2–silicon (p-type, $\rho \approx 10\ \Omega$ cm) structures were studied. Amorphous silicon nitride was obtained at 800 °C from a mixture of $SiCl_4 + NH_3$. The ratio of $SiCl_4/NH_3$ was 1/10. SiO_2, 2 nm thick, was obtained by the thermal oxidation of silicon in nitrous oxide N_2O at 700 °C. Holes in Si_3N_4 were injected and localized at traps when a negative potential was applied to Al. After the polarization of the metal–silicon nitride–silicon oxide–semiconductor (MNOS) structure, a small positive potential was applied to Al. The temperature increased linearly at a rate of 1 K/s. When heated from 300 to 650 K, a depolarization current, caused by the transport of holes from the traps to silicon, was recorded.

The energy diagram of the metal–silicon nitride–silicon oxide–semiconductor (MNOS) structure from Ref. 25 is shown in Fig. 3: without applied voltage [Fig. 3(a)]; at a negative potential on

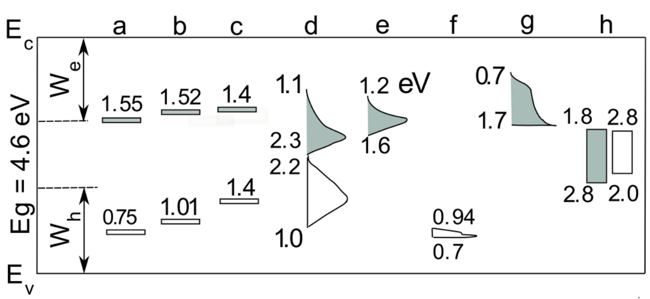

FIG. 2. Discrete and continuous energy levels for electron (W_e) and hole (W_h) traps in a-Si_3N_4 from (a) Ref. 9; (b) Ref. 10; (c) Ref. 11; (d) Ref. 17; (e) Ref. 18; (f) Ref. 19; (g) Ref. 20; (h) Ref. 21. The numbers inside the figure indicate the energy values taken from the corresponding references: (a)–(c) are the discrete trap levels, (d)–(f) are the broadened trap levels, and (g)–(h) are the continuous spectrum of electron and hole traps.

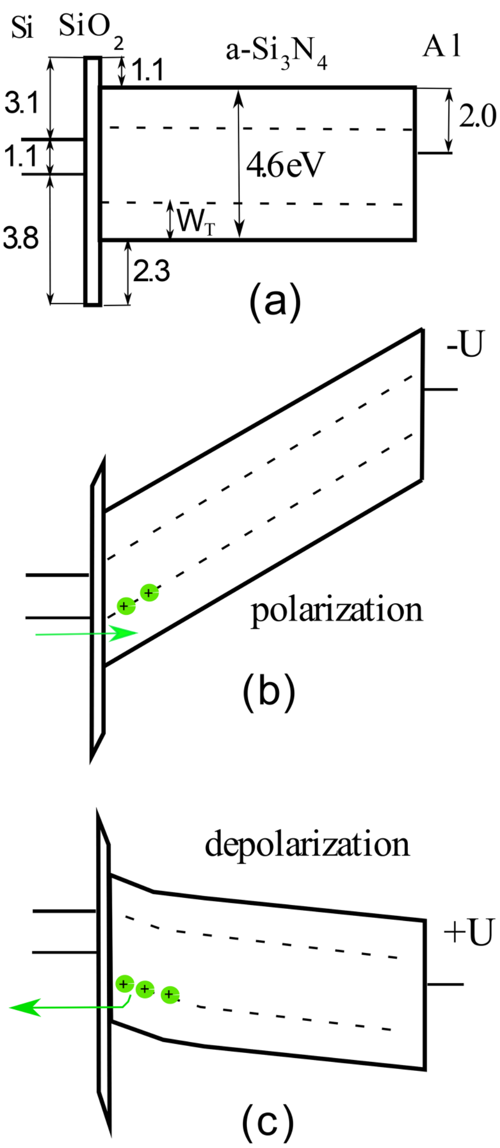

FIG. 3. (a) Band diagram of the MNOS-structure in the absence of voltage on the Al electrode; (b) polarization by holes (at $-U$); (c) thermal depolarization of holes at a positive voltage ($+U$). The dotted line shows the trap energy (W_T).

Al (a-Si_3N_4 polarization) [Fig. 3(b)]; and at a small positive potential on Al (depolarization of a-Si_3N_4) [Fig. 3(c)]. The dotted line inside the a-Si_3N_4 bandgap in Fig. 3 labels the discrete energy levels (W_T) of electron (top) and hole (bottom) traps.

The work considers the three models of the trap energy spectrum in Fig. 4: (1) a trap with a discrete energy level W_T and concentration N_0; (2) a continuous spectrum of traps with three different energy levels and the same concentration $N_1 = N_2 = N_3 = N_0$, and those having three different ionization energies W_T^a, $W_T^b = W_T$ and W_T^c, with $W_T^b - W_T^a = W_T^c - W_T^b = \Delta W$; (3) the spectrum of traps with three different energy levels W_T^i (where $i = a, b, c$) and concentration N_i distributed according to the Gaussian law,

$$N_i = N_0 \exp\left(-\frac{\left(W_T^i - W_T\right)^2}{2\Delta W^2}\right), \tag{1}$$

where N_0 is the maximum concentration and N_i is the concentration corresponding to the energy level W_T^i.

To consider the charge transport, a one-dimensional single-band model is used. The inhomogeneous electric field in a-Si_3N_4 is calculated using the Poisson equation. In this work, in the theoretical description of the experiment, the injection of electrons from the Al electrode is neglected. The model includes the following equations:

$$\frac{\partial p(x,t)}{\partial t} = \frac{1}{e}\frac{\partial j(x,t)}{\partial x} - \sum_i \sigma v p(x,t)(N_i - p_i^t(x,t)) + \sum_i p_i^t(x,t) P_i(x,t), \tag{2}$$

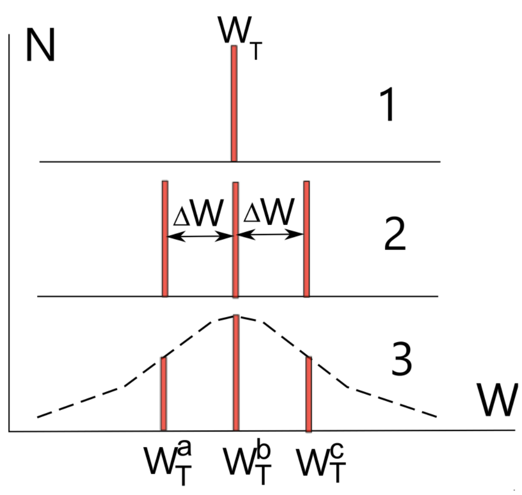

FIG. 4. Options for the traps energy distribution in a-Si_3N_4, where N is the trap concentration, W_T^i (where $i = a, b, c$) is the trap energy in the bandgap: (1) a trap with a discrete energy level ($W_T = W_T^b$); (2) a model of a continuous spectrum of traps with three different energy levels and the same concentration of N_0; (3) with three different energy levels and the concentration of N distributed according to the Gaussian law, where, for ΔW, the values of 0.01, 0.1, and 0.5 eV were used.

$$\frac{\partial p_i^t(x,t)}{\partial t} = \sigma v p(x,t)(N_i(x,t) - p_i^t(x,t)) - p_i^t(x,t)P_i(x,t), \tag{3}$$

$$\frac{\partial F(x,t)}{\partial x} = -\frac{\partial^2 U(x,t)}{\partial x^2} = e\frac{p(x,t) + \sum_i p_i^t(x,t)}{\varepsilon\varepsilon_0}, \tag{4}$$

where index $i = a, b, c$ or only b, depending on the choice of model (Fig. 4), P_i is the trap ionization rate at given electric field values (F), U is the electric potential and temperature (T), σ is the capture cross section, p and p_i^t are the concentration of free and trapped holes, respectively, e is the electron charge, $v = 10^7$ cm/s is the drift velocity,[26–28] and $\varepsilon = 7.0$ is the low-frequency dielectric constant of a-Si_3N_4. The drift velocity of holes is related to the current density by the relation $j = epv$.

To describe the charge transport, the multiphonon trap ionization model is used in Ref. 29 (Fig. 5). For simplicity, the energy diagrams for an electron trap are shown in Fig. 5. Within this model, the trap ionization probability is expressed by

$$\begin{aligned} P &= \sum_{n=-\infty}^{+\infty} \exp\left[\frac{nW_{ph}}{2kT} - S\coth\frac{W_{ph}}{2kT}\right] I_n\left(\frac{S}{\sinh(W_{ph}/2kT)}\right) \times P_i^{\text{tun}}(W_T + nW_{ph}), \\ P_i^{\text{tun}}(W_{\text{tun}}) &= \frac{eF}{2\sqrt{2m^* W_{\text{tun}}}} \exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF} W_{\text{tun}}^{3/2}\right), \\ S &= \frac{W_{\text{OPT}} - W_T}{W_{ph}}, \end{aligned} \tag{5}$$

where W_T is the thermal ionization energy, W_{OPT} is the optical ionization energy of a trap, W_{tun} is the carrier tunneling energy, W_{ph} is the phonon energy, k is the Boltzmann constant, I_n is the Bessel function, and m^* is the tunneling effective mass.

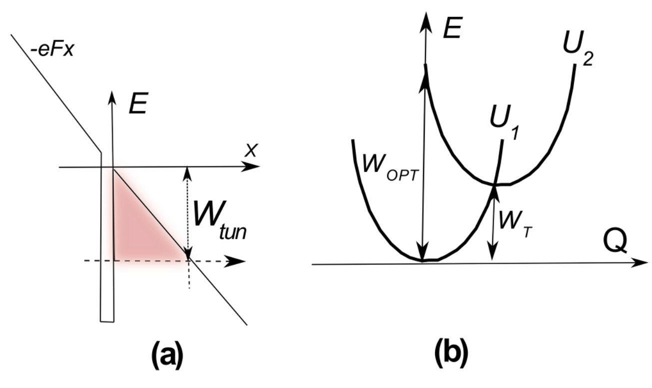

FIG. 5. Multiphonon mechanism of trap ionization; (a) electron tunneling through a potential of zero radius (neutral trap); (b) adiabatic terms: U_1—potential energy of a trap filled with charge carrier, U_2—potential energy of an empty trap, Q—configuration coordinate, W_T and W_{OPT} are the thermal and optical trap ionization energies, respectively, W_{tun}—height of the barrier for tunneling.

As a boundary condition for Eq. (4), the magnitude of the external voltage pulse U applied to the Al contact is used. During the polarization of a-Si_3N_4, injection currents of holes from the Si substrate [Fig. 3(b)] are calculated based on the Fowler–Nordheim mechanism. When depolarizing a-Si_3N_4, to calculate the probability of ionization of holes from traps located near the SiO_2/a-Si_3N_4 interface, the multiphonon ionization theory [formula (5)] is used, taking into account the tunneling of holes through the trapezoidal SiO_2 barrier [Fig. 3(c)].

III. COMPARISON OF EXPERIMENT WITH THE THEORY

A. Trap with a discrete energy level [model 1 (Fig. 4)]

The depolarization current dependence on temperature at different values of the positive voltage on Al is shown in Fig. 6. A satisfactory agreement between the experiment and theory is observed. Both the experiment and calculation predict a shift of the TSD maximum toward low temperatures with the increasing applied voltage. The hole trap parameters obtained from the best agreement between the experiment and calculation are presented in Table I.

B. Continuous spectrum of traps with three different energy levels and the same concentration [model 2 (Fig. 4)]

The TSD of the MNOS structure at the voltage of +4 V (experiment solid line) and the calculation (dashed line) for different ΔW values are shown in Fig. 7.

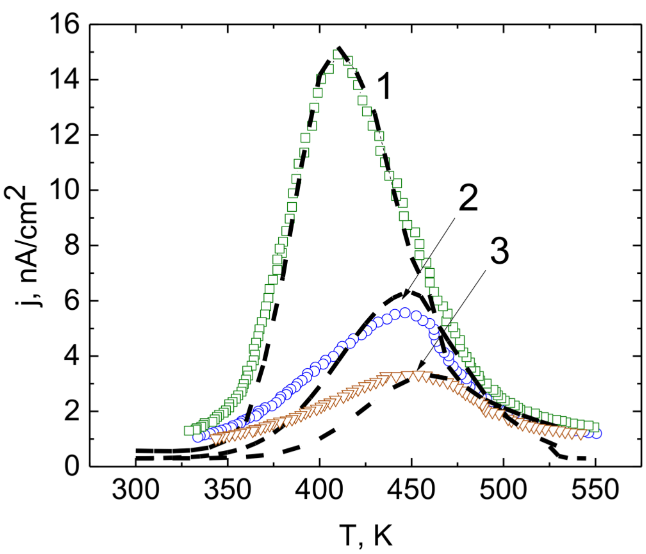

FIG. 6. Dependences of thermally stimulated currents in an MNOS structure with a different accumulated charge (U_{FB}) on the depolarizing voltage value (U): (1) U_{FB} = 3.1 V, U = 4 V, (2) U_{FB} = 2 V, U = 2 V, (3) U_{FB} = 1.7 V, U = 1.5 V. Squares, circles, and triangle—experiment, dashed lines—calculation for a discrete level with thermal ionization energy W_T = 1.15 eV.

TABLE I. Hole trap parameters of in a-Si_3N_4. m_e—free electron mass.

Parameters	W_T (eV)	W_{OPT} (eV)	W_{ph} (eV)	N_0 (cm^{-3})	σ (cm^2)	m^*/m_e
Holes	1.15	2.3	0.06	$4 \cdot 10^{18}$	$5 \cdot 10^{-14}$	0.5

The calculations assume that, in the a-Si_3N_4 bulk, there are traps with three different ionization energies W_T^a, W_T^b and W_T^c, with $W_T^b - W_T^a = W_T^c - W_T^b = \Delta W$, and the same concentrations $N_0 = 4 \times 10^{18}\,cm^{-3}$ (Fig. 4). For the ΔW value, three cases were considered: $\Delta W = 0.01$, 0.1, and 0.5 eV (Fig. 4), with $W_T^b = W_T = 1.15$ eV.

In Fig. 7, it can be seen that increasing the number of energy levels used in calculations does not lead improved agreement with the experiment. For different ΔW values, the calculation predicts the presence of a single peak in the TSD spectrum, which corresponds to the deepest trap. For example, for $\Delta W = 0.5$ eV, the deepest level will correspond to the energy equal to $W_T^c = 1.15 + 0.5 = 1.65$ eV. An increase in ΔW leads to a shift of the only TSD peak toward higher temperatures (Fig. 7). Smaller traps make a minor contribution to the TSD spectrum (Fig. 7). The height of the TSD peaks is the same in all cases due to the same amount of the accumulated charge (U_{FB} = 4 V) captured in the traps.

C. Trap concentration in a-Si_3N_4 distributed according to the Gaussian law depending on the ionization energy [model 3 (Fig. 4)]

A comparison of the TSD experiment with the calculation for the distribution of trap concentrations according to formula (1) at

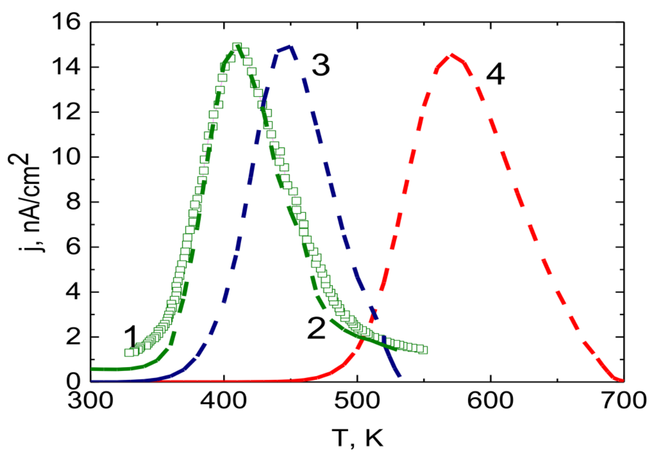

FIG. 7. Comparison of the TSD experiment (1—squares) with the calculation (dashed lines) for the distribution of traps presented in Fig. 4 and the model of a continuous spectrum of traps [model 2 (Fig. 4)], with $W_T^b = 1.15$ eV, for the depolarization voltage of 4 V. Value ΔW (energy distance between trap energy levels): (2) –0.01, (3) –0.1, and (4) –0.5 eV.

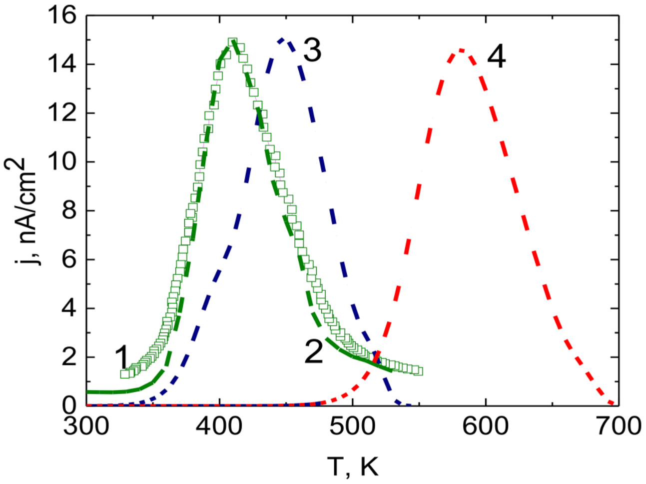

FIG. 8. Comparison of the TSD experiment (1—squares) with the calculation (2, 3, and 4—dashed lines), for the Gaussian distribution of traps [model 3 (Fig. 4)] with $W_T^b = 1.15$ eV at the depolarization voltage of 4 V. Dispersion values (energy distance between trap energy levels) ΔW: (2) −0.01, (3) −0.1, and (4) −0.5 eV.

$N_0 = 4 \times 10^{18}$ cm^{-3} [Fig. 4, option (3)], is shown in Fig. 8. For traps, three ionization energies differing by $\Delta W = 0.01$, 0.1, and 0.5 eV were considered.

It can be seen in Fig. 8 that, with the increasing ΔW, there is a shift in the TSD dependences toward higher temperatures. The dominant contribution to the TSD spectrum comes mainly from the deep traps with the energy $W_T^c = 1.65$ eV. Although the concentration of traps with the energy $W_T^b = 1.15$ eV exceeds the concentration of traps with the energy $W_T^c = 1.65$ eV, small traps do not contribute to the TSD spectrum. The small contribution of traps with an energy of 1.15 eV to the TSD spectrum is due to the fact that, in the polarization mode of the MNOS structure, their filling is small, compared to the filling of traps with an energy of 1.65 eV.

IV. DISCUSSION

In Ref. 23, using the example of the Frenkel effect,[30] it was theoretically demonstrated that, with the increasing depolarization voltage, the TSD maximum shifts toward low temperatures. This effect is explained by the fact that, in an electric field, the trap ionization energy, according to the Frenkel model, is decreased.[30] In this work, the multiphonon ionization theory is used to describe the trap ionization probability. The multiphonon ionization theory also predicts that,[29] in an electric field, the trap ionization probability is increased due to an increase in the barrier tunneling transparency. An increase in the trap ionization probability in an electric field leads to a shift in the TSD maximum (Fig. 6), i.e., with an increase in the depolarization voltage toward low temperatures.

Experiments of TSD are satisfactorily described by the multiphonon ionization theory under the assumption that a-Si_3N_4 contains traps with a discrete energy $W_T = 1.15$ eV. The calculation of TSD for the case of a continuous and Gaussian spectrum of traps does not lead to an improvement in the agreement the between experiment and calculation (Figs. 7 and 8). Both in the case when a-Si_3N_4 contains traps with equal concentrations, but with different ionization energies, and in the case of traps distributed according to the Gaussian law depending on the energy, the calculation predicts similar TSD dependences (Figs. 7 and 8). In all cases, in the presence of traps with different energies in a-Si_3N_4, a single peak was observed in the TSD, which corresponds to traps with the maximum ionization energy (deepest trap). The negligible trap contribution shallow to the TSD spectrum is due to the fact that, in the polarization mode of the MNOS-structure, their filling is small, compared to deeper traps.

Experiments discussed in the literature point to different energies of traps in a-Si_3N_4 (Fig. 2).[9–21] This difference may be due to two reasons. First, the trap energy may depend on the a-Si_3N_4 synthesis technology. Second, the energy and spectrum of traps may depend on the model describing the trap's ionization. For example, in Ref. 10, when considering the delocalization of electrons, the thermal ionization of traps is considered, and in Ref. 20, when considering the delocalization of electrons, the tunneling mechanism of trap ionization is considered. In this work, it was established that the studied a-Si_3N_4 compound contains discrete traps with an energy of 1.15 eV. In Ref. 10, the hole trap energy was determined as 1.01 ± 0.03 eV. This value is close to the trap energy obtained in this work. The broadening of the discrete trap level in a-Si_3N_4, according to our data, does not exceed 0.01 eV. This means that the broadening of the trap level due to the fluctuations in the Si–N bond length and due to the fluctuations in the N–Si–N and Si–N–Si angles, i.e., due to the absence of long-range order in amorphous a-Si_3N_4, is insignificant. Thus, the interpretation of the charge transport in a-Si_3N_4 based on the discrete trap spectrum is correct.[11] The discrete trap spectrum model can be used to simulate the storage properties of flash memory devices based on a-Si_3N_4.

V. CONCLUSION

In this work, the TSD currents in MNOS structures were studied experimentally and theoretically. The experiment is satisfactorily described by the theory of multiphonon ionization of traps with the discrete level of 1.15 eV. The broadening of the discrete trap level in a-Si_3N_4, according to our data, does not exceed 0.01 eV. The calculation of TSD for the case of a continuous and Gaussian spectrum of traps does not lead to an improvement in the agreement between the experiment and calculation.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, under Grant No. 22-19-00369 (sample synthesis and TSD measurements) and the state contract with the ISP SB RAS Program No. FWGW-2021-0003 (modeling TSD measurements).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yu. N. Novikov: Conceptualization (equal); Data curation (lead); Investigation (equal); Methodology (equal); Writing – original draft (lead). **V. A. Gritsenko:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Project administration (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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