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Exponentially strong leakage current increase in the proton-irradiated silicon nitride

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ABSTRACT

The charge transport in a strong electric field in proton-irradiated amorphous silicon nitride films with different irradiation doses is studied experimentally and theoretically. The leakage current increases with the increasing irradiation dose. The Frenkel model and the model of overlapping Coulomb potentials do not explain the charge transport mechanism. The charge transport mechanism in the initial Si_3N_4 film is explained by the Makram-Ebeid and Lannoo multiphonon isolated trap ionization model. The increase in the leakage current during irradiation is quantitatively described by the phonon-assisted tunneling of electrons between neighboring traps. Such a model explains the exponentially strong leakage current scatter in non-stoichiometric SiN_x films.

Amorphous silicon nitride (Si_3N_4) has a high (10^{18}–10^{21} cm^{-3}) concentration of electron and hole traps and has a memory effect [1]. The memory effect consists in the electron localization in deep (≈1.5 eV) traps, the electron lifetime in the localized state is 10 years at 85 °C. The memory effect in Si_3N_4 underlies the operating principle of modern flash memory [2]. The intensive study of the memory effect led to the fact that amorphous Si_3N_4 is currently a model material in the study of electron localization processes and in the study of charge transport in silicon device dielectrics [3,4].

The enrichment of Si_3N_4 film with excess silicon ($SiN_{x<4/3}$) leads to exponential increase in the conductivity of SiN_x (by 10 orders of magnitude) with a decreasing x [4,5]. In [4], it was shown that irradiation with Zn ions also leads to an increase in the Si_3N_4 conductivity. The present work is devoted to studying the effect of proton irradiation of Si_3N_4 on conductivity and to establishing the cause of the increase in the Si_3N_4 conductivity.

The 90 nm thick Si_3N_4 films were deposited from a mixture of SiH_4 and NH_3 at 850 °C on an n-type silicon substrate with the (100) orientation, 10 Ohm*cm resistance and the SiH_4/NH_3 ratio of 0.03. The Si_3N_4 film thickness was determined using a laser ellipsometer. The proton energy during implantation was 30 keV. The deposited aluminum contacts with an area of 5×10^{-3} cm^2 served as upper electrode. The current density *versus* field (*lgj-F*) characteristics were measured using a Keithley 2400 device. The measurements were performed at room temperature. The current density *versus* reverse temperature (j-1000/T) characteristics were measured at 4 MV/cm using Keithley 2400 device with a Linkam LTS420E cell.

In Fig. 1(a) are the experimental *lgj-F* dependences of initial Si_3N_4 film and proton-irradiated Si_3N_4 films with different irradiation doses. Irradiation of Si_3N_4 with protons leads to an increase in the leakage current at a fixed electric field. At the maximum irradiation dose of 10^{16} cm^{-2}, the leakage current increases by four orders of magnitude (Fig. 1 (a)). In Fig 1(b) the similar curve slope of j-1000/T for initial Si_3N_4 film and proton-irradiated Si_3N_4 films indicate that after irradiation the ionization trap energy did not change.

At present, the dominant point of view is that the dielectric conductivity is limited by the Frenkel effect [6–14]. The Frenkel effect consists of a decrease in the Coulomb trap ionization energy in an electric field (Fig. 1(c)).

In our model, the space charge of the filled traps in the dielectric is neglected. The current density in this approximation is given by the expression:

$$j = eN^{2/3}P \tag{1}$$

Here P – ionization probability of Coulomb trap and N – trap concentration.

The ionization probability of an isolated Coulomb trap in an electric field F is given by the expression [6,7]:

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$$P_F = \nu \exp\left(-\frac{W - \beta\sqrt{F}}{kT}\right); \beta = \sqrt{\frac{e^3}{\pi\varepsilon_\infty\varepsilon_0}}. \quad (2)$$

Here W – Coulomb trap ionization energy, β – Frenkel constant, $\varepsilon_\infty = n^2 = 4.0$ – high frequency permittivity, n – refractive index Si_3N_4 and $\nu = W/h$ – attempt-to-escape factor.

The Frenkel effect was initially predicted for an isolated Coulomb trap; such a case is realized at a low (10^{18}–10^{19} cm^{-3}) trap concentration, when the distortion of the Coulomb potential due to neighboring traps can be neglected (Fig. 1(a)). The slope of the *lgj-F* dependence of initial Si_3N_4 film is in a good agreement with the value of the experimentally measured high-frequency permittivity $\varepsilon_\infty = 4.0$. With the value of the frequency factor determined by the Einstein formula $\nu = W/h = 3.87 \times 10^{14}$ s^{-1}, the trap concentration, according to the simulating by the Frenkel effect, has a value of $N = 8.8 \times 10^4$ cm^{-3}. This value is many orders of magnitude smaller than the typical trap concentration in dielectrics (10^{18}–10^{21} cm^{-3}) [12]. In addition, in Fig 1(b) current density temperature dependence at 4 MV/cm simulated by the Frenkel model describe experimental data only at room temperature. Thus, the Frenkel model does not describe the charge transport mechanism in the initial Si_3N_4 film. The Frenkel model also does not describe the charge transport in proton-irradiated Si_3N_4, films since the trap concentration obtained using the Frenkel model is also many orders of magnitude smaller than the typical trap concentration in dielectrics (Table 1).

The increase in the leakage current after the proton irradiation of Si_3N_4 in the Frenkel model can naturally be explained by an increase in the trap concentration. An increase in the concentration of Coulomb traps leads to an overlap of the Coulomb potentials of neighboring traps, a decrease in the ionization barrier, (Fig. 1(d) Hill-Adachi (H-A) model [14,15]) and an exponentially strong increase in the trap ionization probability. The expression for the ionization probability in the H-A model has the form:

$$P = 2\nu \exp\left(-\frac{W - \frac{e^2}{\pi\varepsilon_\infty\varepsilon_0 a}}{kT}\right)\sinh\left(\frac{eFa}{2kT}\right) \quad (3)$$

Here a is an average distance between traps and it is related to the trap concentration by the following expression: $N = a^{-3}$.

Table 1
Simulation parameters of the theoretical Frenkel, Hill-Adachi (H-A), ME-L and N-G models at room temperature 297 K, Coulomb trap ionization energy 1.6 eV, thermal trap ionization energy 1.6 eV and optical trap ionization energy 3.2 eV for different proton irradiation doses.

Dose	Frenkel	H-A	ME-L	N-G
0	ε_∞ =4.0 $N = 8.8 \times 10^4$ cm^{-3} ν =3.9 × 10^{14} s^{-1}	ε_∞ =4.2 $N = 1.9 \times 10^{20}$ cm^{-3} ν =1.9 × 10^2 s^{-1}	$N = 5.0 \times 10^{18}$ cm^{-3} m^*=0.41 m_e	$N = 1.9 \times 10^{20}$ cm^{-3} m^*=1.55 m_e
10^{14} cm^{-2}	ε_∞ =4.0 $N = 0.7$ cm^{-3} ν =3.9 × 10^{14} s^{-1}	ε_∞ =4.2 $N = 2.1 \times 10^{20}$ cm^{-3} ν =3.7 × 10^3 s^{-1}	$N = 5.1 \times 10^{20}$ cm^{-3} m^*=0.41 m_e	$N = 2.1 \times 10^{20}$ cm^{-3} m^*=1.3 m_e
10^{15} cm^{-2}	ε_∞ =5.6 $N = 2.1 \times 10^6$ cm^{-3} ν =3.9 × 10^{14} s^{-1}	ε_∞ =4.2 $N = 3.1 \times 10^{20}$ cm^{-3} ν =9 × 10^3 s^{-1}	$N = 5.0 \times 10^{23}$ cm^{-3} m^*=0.41 m_e	$N = 3.1 \times 10^{20}$ cm^{-3} m^*=1.11 m_e
10^{16} cm^{-2}	ε_∞ =8.9 $N = 4.5 \times 10^{11}$ cm^{-3} ν =3.9 × 10^{14} s^{-1}	ε_∞ =4.2 $N = 4.5 \times 10^{20}$ cm^{-3} ν =9 × 10^3 s^{-1}	$N = 4.9 \times 10^{26}$ cm^{-3} m^*=0.41 m_e	$N = 4.5 \times 10^{20}$ cm^{-3} m^*=0.8 m_e

Expression (3) allows us to determine the trap concentration from the slope of the *lgj-F* dependence. The experimental *lgj-F* dependences of irradiated Si_3N_4 are satisfactorily described by the H-A model at the reasonable high-frequency permittivity value ε_∞ =4.2 (Fig. 1(a) and Fig 1(b)). The leakage current increase in the irradiated Si_3N_4 film is explained by an increase in the trap concentration N in the H-A model (Fig 1(a) and Fig 1(b)). However, agreement with the experiment is observed at an anomalously small, non-physical value of the attempt-to-escape factor (Table 1). Thus, the H-A model does not describe the conductivity increase in the of proton-irradiated Si_3N_4.

In [16,17], it was shown that the Si_3N_4 conductivity is described by multiphonon trap ionization. The theory of multiphonon trap ionization was developed in [18–21]. In the Makram-Ebeid and Lannoo (ME-L)

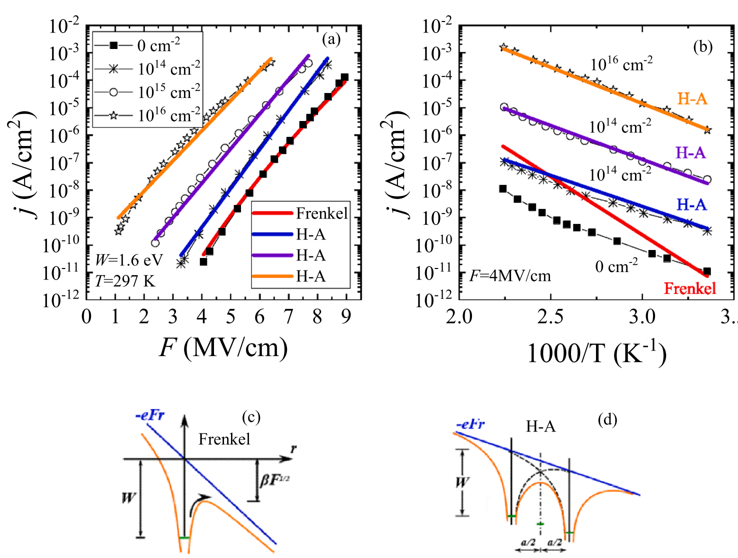

Fig. 1. (a) Experimental *lgj-F* dependences of initial Si_3N_4 film and proton-irradiated Si_3N_4 films with different doses of 10^{14} cm^{-2}, 10^{15} cm^{-2} and 10^{16} cm^{-2} at a positive potential on aluminum at room temperature. (b) Experimental *j*-1000/*T* dependences of initial Si_3N_4 film and proton-irradiated Si_3N_4 films with different doses of 10^{14} cm^{-2}, 10^{15} cm^{-2} and 10^{16} cm^{-2} at 4 MV/cm. The theoretical curve for the initial Si_3N_4 film was calculated using the Frenkel model. The theoretical curves for proton-irradiated Si_3N_4 films were calculated using the Hill-Adachi (H-A) model. (c) Potential diagram of an isolated Coulomb trap in an electric field, in case of a low trap concentration (Frenkel model). (d) Potential diagram of overlapping Coulomb traps in an electric field, in case of a high trap concentration (H-A model).

model [18], the probability of multiphonon isolated trap ionization is given by the expression:

$$P = \sum \exp\left(\frac{nW_{ph}}{2kT} - \frac{W_{opt} - W_t}{W_{ph}} \coth\frac{nW_{ph}}{2kT}\right) I_n\left(\frac{W_{opt} - W_t}{W_{ph}\sinh(W_{ph}/2kT)}\right) P_i(W_t + nW_{ph}), \quad (4)$$

$$P_i = \frac{eF}{2\sqrt{2m^*(W_t + nW_{ph})}} \exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF}(W_t + nW_{ph})^{3/2}\right). \quad (5)$$

Here, W_t – thermal trap ionization energy, W_{opt} – optical trap ionization energy, W_{ph} – phonon energy, m^* – electron effective mass and I_n – Bessel function.

In Fig. 2(a) are the experiment and simulation using the ME-L model of multiphonon isolated trap ionization. In Fig. 2(e) are schematic representation of the ME-L model.

The experiment for unirradiated Si_3N_4 is satisfactorily described by the ME-L model for the thermal trap ionization energy of 1.6 eV and the optical trap ionization energy of 3.2 eV at the trap concentration of 5.0×10^{18} cm^{-3} and the effective mass of $m^*=0.41\ m_e$ (Fig. 2(a) and Fig. 2(c)). The ME-L model has a good agreement with experimental j-1000/T, but obtained trap concentration values from the ME-L model simulation for proton-irradiated Si_3N_4 are abnormally high (Fig. 2(c) and Table1). The applicability trap concentration value range of the isolated trap ionization model is 10^{18}–10^{19} cm^{-3}. For irradiated Si_3N_4, the slope of the experimental *lgj-F* dependences differs significantly from the calculated dependences (Fig. 2(a)). Therefore, the ME-L model describe the charge transport only in the initial Si_3N_4.

In the contributions by Nasyrov and Gritsenko [22] the multiphonon trap ionization theory was developed for the high trap concentration case. At a low trap concentration, their ionization occurs to the conduction band (Fig. 2(f)). At high trap concentrations, when the distance a between traps is small, an electron tunnels from a filled trap to a neighboring empty trap (Fig. 2(f)).

The probability of phonon-assisted tunneling between neighboring

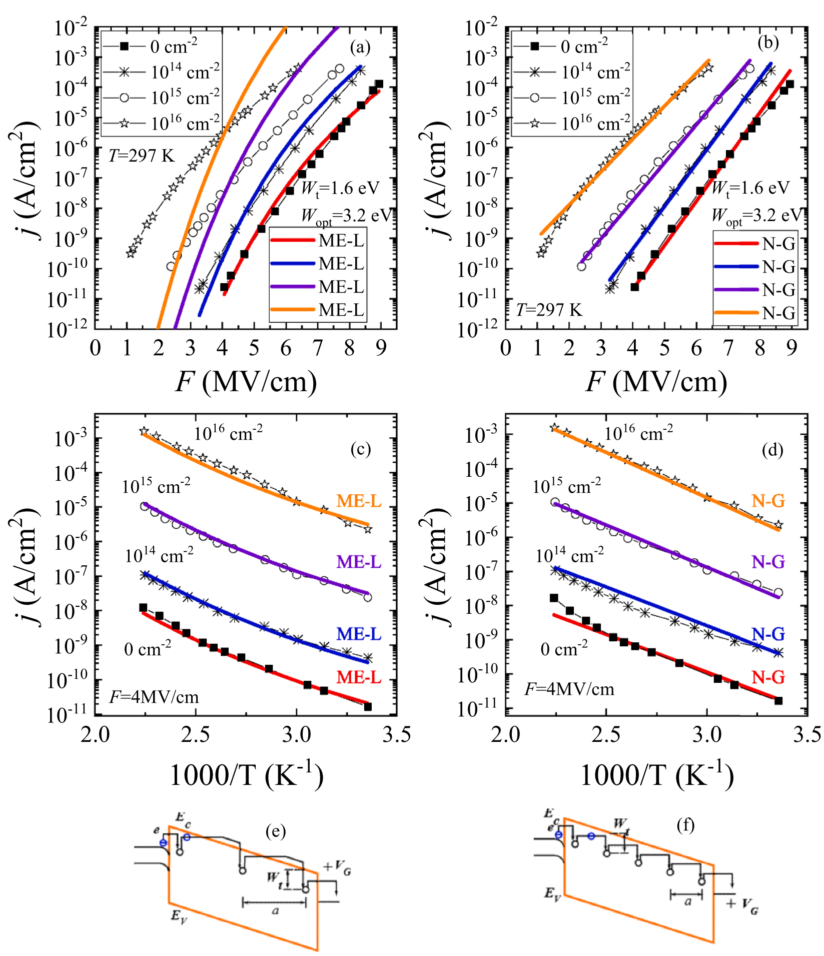

Fig. 2. (a, b) Experimental *lgj-F* dependences of the initial Si_3N_4 film and proton-irradiated Si_3N_4 films with different doses of 10^{14} cm^{-2}, 10^{15} cm^{-2} and 10^{16} cm^{-2} at a positive potential on aluminum at room temperature. The theoretical curves *lgj-F* for the initial and proton-irradiated Si_3N_4 films were calculated using (a) the Makram-Ebeid and Lannoo (ME-L) model and (b) Nasyrov-Gritsenko (N-G) model. (c, d) Experimental j-1000/T dependences of initial Si_3N_4 film and proton-irradiated Si_3N_4 films with different doses of 10^{14} cm^{-2}, 10^{15} cm^{-2} and 10^{16} cm^{-2} at 4 MV/cm. The theoretical j-1000/T curves for the initial and proton-irradiated Si_3N_4 films were calculated using (c) the Makram-Ebeid and Lannoo (ME-L) model and (d) Nasyrov-Gritsenko (N-G) model. Schematic representation of the (e) ME-L multiphonon isolated trap ionization model and (f) N-G model of phonon-assisted tunneling between neighboring traps.

traps in the Nasyrov-Gritsenko (N-G) model is given by the expression [22]:

$$P = \frac{2\sqrt{\pi}\hbar W_t}{m^* a^2 \sqrt{2kT(W_{opt} - W_t)}} \exp\left(-\frac{W_{opt} - W_t}{kT}\right) \exp\left(-\frac{2a\sqrt{2m^* W_t}}{\hbar}\right) \sinh\left(\frac{eFa}{2kT}\right) \quad (6)$$

The experiment is well described by the N-G model for proton-irradiated Si_3N_4 (Fig. 2(b), Fig. 2(d), Table 1). The *lgj-F* dependences of the initial Si_3N_4 film are described by the N-G theory of phonon-assisted tunneling between neighboring traps at the thermal trap ionization energy $W_t = 1.6$ eV and at the optical trap ionization energy $W_{opt} = 3.2$ eV. However, the N-G modeling gives an overestimated trap concentration of 1.9×10^{20} cm^{-3} and an effective mass value of m^*=1.55 m_e for the initial Si_3N_4 film. In additional, In Fig. 2(d) the experimental data and simulated curves are starting to diverge from 400 K and higher temperature for the initial Si_3N_4 film.

The overestimated effective mass for Si_3N_4 irradiated with doses of 10^{14} cm^{-2} and 10^{15} cm^{-2} may be due to the simplified assumption of no space charge on the traps when the current flows. A more accurate model should use the Shockley-Reed-Hall and Poisson equations.

To explain the leakage currents of Si_3N_4 before and after proton irradiation, four trap ionization models are used in this work. The ME-L model describes the charge transport in the initial Si_3N_4 film before proton irradiation at a low trap concentration. The N-G model quantitatively describes the increase in the leakage current in the Si_3N_4 structure after proton irradiation with different doses at a high trap concentration. The trap concentration in the N-G model is the same as in the H-A model of overlapping Coulomb traps. One of the differences between the H-A and N-G models is the ionization mechanism. The other difference between the H-A and N-G models is that the H-A model assumes the presence of positively charged Coulomb traps, but the N-G model assumes the presence of neutral traps.

The Nasyrov-Gritsenko model of phonon-assisted tunneling between neighboring traps describes the increase in the leakage current upon the proton irradiation of Si_3N_4. The increase in the leakage current upon the proton irradiation is explained by the increase in the trap concentration. The increase in the trap concentration leads to an exponentially strong increase in the leakage current. It seems to us that the Nasyrov-Gritsenko model explains the exponentially strong leakage current spread in SiN_x [4,5], SiO_x [23,24] and AlO_x [25] films.

CRediT authorship contribution statement

A.A. Gismatulin: Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **V.A. Gritsenko:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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