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Multiphonon Ionization of Deep Centers in Amorphous Silicon Nitride: Experiment and Numerical Simulations

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The conductivity of amorphous silicon nitride has been studied experimentally in a wide range of electric fields and temperatures. The experimental results are in a quantitative agreement with the theory of multiphonon ionization of deep centers for the bipolar model of conductivity. The best agreement between the experiment and the calculation has been obtained for the same parameters of deep electron and hole centers. © *2003 MAIK "Nauka/Interperiodica".*

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The majority of amorphous dielectrics, such as Si_3N_4, Ce_3N_4, BN, Ta_2O_5, HfO_2, Y_3O_3, TiO_2, etc., contain a high density of deep centers (traps). The conductivity of such dielectrics in strong electric fields (10^6–10^7 V/cm) is limited by the ionization of deep centers. Silicon nitride is a dielectric in which that is most comprehensively studied from the viewpoint of the mechanism of charge transfer.

Amorphous silicon nitride (Si_3N_4) is characterized by a high density (>10^{19} cm^{-3}) of electron and hole traps with a giant confinement time of electrons and holes in a localized state (>10 years at 300 K) [1]. Currently, it is commonly accepted that the ionization of deep centers in Si_3N_4 is confined to the Frenkel effect [2–5]. However, it was demonstrated in [4–8] that the interpretation of Si_3N_4 conductivity within the Frenkel model gives an anomalously small value of the frequency factor $\nu \approx 10^6$–10^7 s^{-1}. The frequency factor was estimateed in the original paper by Frenkel at a level of $\nu \approx 10^{15}$ s^{-1} [9]. Moreover, the formal agreement with the modified Frenkel model that takes into account tunnel ionization can be obtained only at an anomalously large value of the effective tunneling mass $m^* = 4m_e$ [8]. At the same time, experiment gives a value of the effective tunneling mass in silicon nitride close to $m^* = 0.4m_e$ [10]. As distinct from dielectrics, the ionization of deep centers in semiconductors is interpreted within the theory of multiphonon ionization [11].

In [8], experimental results on the conductivity of metal nitride–oxide–semiconductor (MNOS) structures were quantitatively compared with the theory of multiphonon ionization for the unipolar model of conductivity, which takes into account only electron injection from silicon and does not take into account hole injection from the metal, see Fig. 1a. On the other hand, in this work experimental results are compared with the more general bipolar model, in which the injection of electrons from silicon, the injection of holes from the metal, and the recombination of free electrons with localized electrons and free holes with localized electrons are taken into account, see Fig. 1b. The goal of this work is to study experimentally the mechanism of charge transfer in Si_3N_4 over a wide range of temperatures and fields and to compare quantitatively the experiment with the calculation based on the bipolar

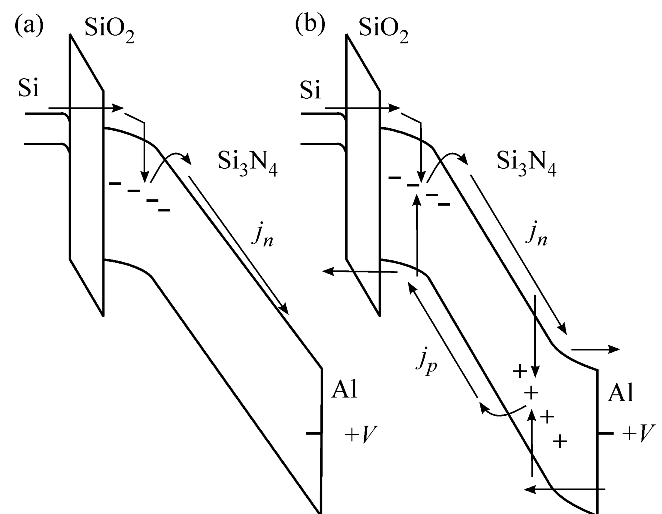

Fig. 1. Energy diagram for (a) unipolar and (b) bipolar models of conductivity for an MNOS structure at a positive voltage on an aluminum electrode. Symbols (–) and (+) mark respectively electrons and holes captured by a trap.

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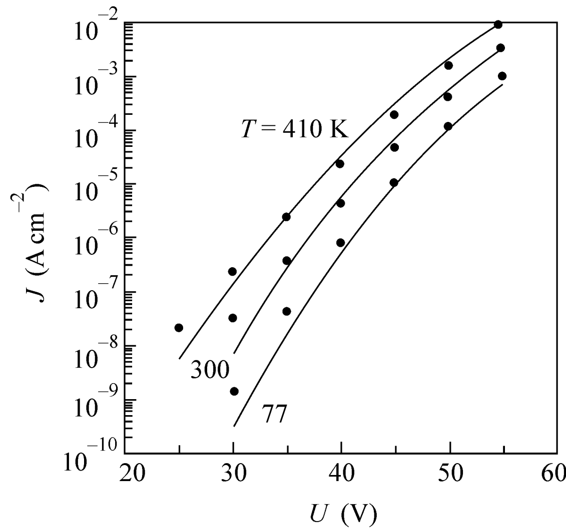

Fig. 2. Experimental (dots) and calculated (solid lines) current–voltage characteristics for the model of the multiphonon ionization of traps in Si_3N_4 at a positive voltage on an aluminum electrode. The calculation was carried out for the same parameters of electron and hole traps $\sigma^e = \sigma^h = \sigma_r = 5 \times 10^{-13}$ cm^2, $W_t^e = W_t^h = W_t = 1.7$ eV, $W_{\rm opt}^e = W_{\rm opt}^h = W_{\rm opt} = 2.7$ eV, $W_{\rm ph}^e = W_{\rm ph}^h = W_{\rm ph} = 0.045$ eV, and $N_t^e = N_t^h = N_t = 7 \times 10^{19}$ cm^{-3}.

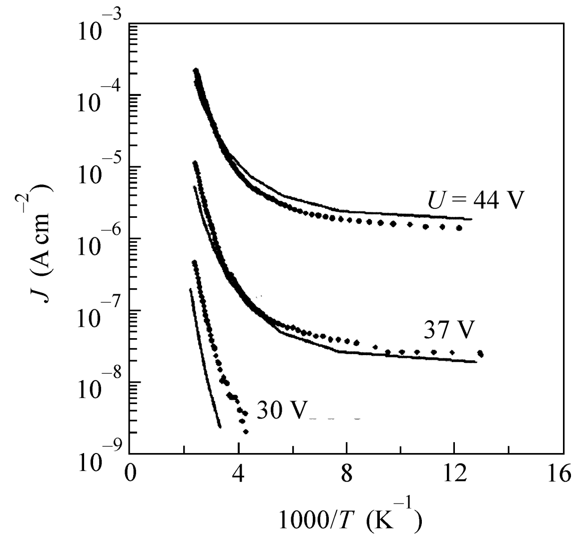

Fig. 3. Experimental (dots) and calculated (solid lines) temperature dependences of the current for the model of the multiphonon ionization of traps for a positive voltage on an aluminum electrode. The calculation was carried out for the same parameters of electron and hole traps $\sigma^e = \sigma^h = \sigma_r = 5 \times 10^{-13}$ cm^2, $W_t^e = W_t^h = W_t = 1.7$ eV, $W_{\rm opt}^e = W_{\rm opt}^h = W_{\rm opt} = 2.7$ eV, $W_{\rm ph}^e = W_{\rm ph}^h = W_{\rm ph} = 0.045$ eV, and $N_t^e = N_t^h = N_t = 7 \times 10^{19}$ cm^{-3}.

conductivity model and the multiphonon mechanism of trap ionization in silicon nitride.

Samples of MNOS structures were manufactured on a p-type silicon substrate with a resistivity of 20 Ω cm grown using the Czochralski method. A thin, tunnel-transparent oxide layer 18-Å thick was grown at a temperature of 760°C. Silicon nitride 670-Å thick was obtained at a temperature of 700°C by the deposition method in a low-pressure reactor. The SiH_2Cl_2/NH_3 ratio was 0.1. Aluminum electrodes with an area of 5×10^{-3} cm^2 were sputtered through a mask.

Current–voltage characteristics (Fig. 2) were measured experimentally at different temperatures, and temperature dependences of the current (Fig. 3) were measured for different voltages. The experimental dependences were obtained in a cryostat cooled by liquid nitrogen with controlled temperature in the range 77–450 K. The current–voltage characteristics were measured with voltage varied at a rate of 0.02 V/s. The heating rate of samples was ~5 K/min. All the measurements were carried out for positive voltages on the gate. At this voltage polarity, both the injection of electrons from the silicon substrate and the injection of holes from aluminum take place.

A one-dimensional bipolar model of Si_3N_4 conductivity was used for comparison with experiment. Previously this model was used in [12]. Charge transfer was described with the use of the Shockley–Read–Hall equation and the Poisson equation taking into account the nonuniform electric field distribution in silicon nitride

$$\frac{\partial n(x,t)}{\partial t} = \frac{1}{e}\frac{\partial j(x,t)}{\partial x} - \sigma^e \nu n(x,t)(N_t^e - n_t(x,t)) + n_t(x,t)P(x,t) - \sigma_r \nu n(x,t)p_t(x,t), \quad (1)$$

$$\frac{\partial n_t(x,t)}{\partial t} = \sigma^e \nu n(x,t)(N_t^e + n_t(x,t)) - n_t(x,t)P(x,t) - \sigma_r \nu n(x,t)n_t(x,t), \quad (2)$$

$$\frac{\partial p(x,t)}{\partial t} = \frac{1}{e}\frac{\partial j_p(x,t)}{\partial x} - \sigma^h \nu p(x,t)(N_t^h - p_t(x,t)) + p_t(x,t)P(x,t) - \sigma_r \nu p(x,t)n_t(x,t), \quad (3)$$

$$\frac{\partial p_t(x,t)}{\partial t} = \sigma^h \nu p(x,t)(N_t^h - p_t(x,t)) - p_t(x,t)P(x,t) - \sigma_r \nu p(x,t)n_t(x,t), \quad (4)$$

$$\frac{\partial F}{\partial x} = -e\frac{(n_t(x,t) - p_t(x,t))}{\varepsilon\varepsilon_0}. \quad (5)$$

Here, n and n_t are the concentrations of free and trapped electrons, p and p_t are respectively the concentrations of free and trapped holes, N_t^e and N_t^h are the concentra-

tions of electron and hole traps, $F(x, t)$ is the local electric field, e is the electron charge, $\sigma^{e,h}$ is the capture cross section of a trap, σ_r is the recombination cross section between free and trapped carriers of opposite sign, v is the drift velocity, and $\varepsilon = 7.5$ is the low-frequency permittivity of Si_3N_4. The following values were used in this work for the capture and recombination cross sections $\sigma^e = \sigma^h = \sigma_r = 5 \times 10^{-13}$ cm^2[6, 7, 13]. The drift velocity of electrons is related to the current density by the equation $j = env$. The multiphonon ionization model [11, 14] was used for the ionization probability P of a trap in Si_3N_4

$$P = \frac{eF}{2\sqrt{2m^*W_{\rm opt}}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m}}{\hbar eF}W_{\rm opt}^{3/2} + 4\frac{m^*}{\hbar^2}\frac{W_{\rm ph}}{F^2}W_{\rm opt}(W_{\rm opt}-W_t)\coth\frac{W_{\rm ph}}{2T}\right), \quad (6)$$

where $W_{\rm opt}$ and W_t are the optical and thermal ionization energies of a trap, $W_{\rm ph}$ is the phonon energy, m^* is the effective mass of a carrier. The same effective masses equal to $0.5m_0$ (where m_0 is the free electron mass) were chosen in modeling for electrons and holes. The electron and hole injection from the silicon substrate and aluminum electrode, respectively, was calculated based on the Fowler–Nordheim mechanism. We carried out two series of experiments, in one of which the current–voltage characteristic was recorded at a fixed sample temperature, and the temperature dependence of the current through the MNOS was recorded in the second series at a constant applied voltage. The current–voltage characteristics (Fig. 2) were measured at temperatures $T = 77$, 300, and 410 K in the voltage range 30–55 V, which corresponds to average electric fields of ~(4–8) × 10^6 V/cm in silicon nitride. It is evident in the figure that the current increases exponentially with increasing voltage on the aluminum electrode.

The temperature dependences of the current were measured in the temperature range 77–410 K for voltages of 44, 37, and 30 V and were plotted on the Arrhenius coordinates $\ln(j) - T^{-1}$ (Fig. 3). The figure demonstrates that the current weakly depends on the temperature at $T < 200$ K. The weak temperature dependence of the current points to the tunneling mechanism of trap ionization. The same behavior of the measured currents with temperature was observed previously in [2, 3].

The direct tunneling of carriers through the triangular barrier without the participation of phonons is the main mechanism of trap ionization at low temperatures. The ionization probability in the presence of an electric field is given by the equation [15]

$$P = \frac{eF}{2\sqrt{2m^*W_{\rm opt}}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF}W_{\rm opt}^{3/2}\right). \quad (7)$$

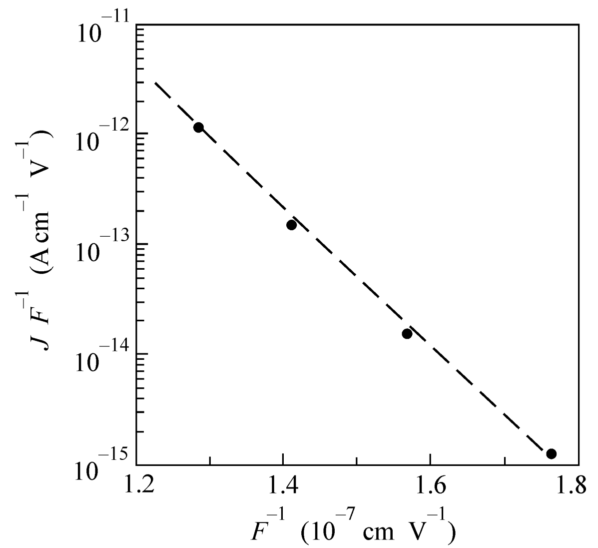

Fig. 4. Experimental dependence j/F versus $1/F$ for the temperature $T = 77$ K constructed on a semilogarithmic scale.

The lowest field $F_{\rm min}$ necessary for such tunneling is determined from the relationship

$$F_{\rm min} = \frac{2\omega\sqrt{2m^*W_{\rm ph}}}{e}, \quad (8)$$

where ω is the frequency of the trap "nucleus," which can be estimated from the relationship $\omega \approx W_{\rm ph}/\hbar$. The estimation gives $F_{\rm min} = 5 \times 10^6$ V/cm.

The experimental current–voltage characteristic constructed on the $\ln(j/F)$–$1/F$ coordinates for the temperature $T = 77$ K and electric fields higher than 5×10^6 V/cm is shown in Fig. 4. The average field $F = V/d$ (V is voltage, and d is the nitride thickness) is plotted in Fig. 4. On these coordinates, the rectification of the experimental curve is observed. The optical energy of the trap $W_{\rm opt} = 2.5$ eV was estimated by the slope of the curve for $m^* = 0.5$.

It was found that the best agreement with the experiment is obtained for the same parameters of electron and hole traps: $W_t^e = W_t^h = W_t = 1.7$ eV, $W_{\rm opt}^e = W_{\rm opt}^h = W_{\rm opt} = 2.7$ eV, $W_{\rm ph}^e = W_{\rm ph}^h = W_{\rm ph} = 0.045$ eV, and $N_t^e = N_t^h = N_t = 7 \times 10^{19}$ cm^{-3}. The current–voltage characteristics calculated for temperatures of 77, 300, and 410 K are shown in Fig. 2 (solid lines), and temperature dependences of the current for voltages U (44, 37, and 30 V) on the aluminum electrode are shown in Fig. 3 (solid lines). The largest discrepancy between the calculated and experimental data was observed for voltages less than 35 V. This discrepancy can be explained by slow current relaxation in silicon nitride, whose nature remains unclarified [16]. The value $W_{\rm opt} = 2.5$ eV estimated by the slope of the current–voltage characteristic (Fig. 4) turned out to be smaller than the value

W_{opt} = 2.7 eV obtained from an accurate simulation of the experiment (Fig. 2 and Fig. 3). This small discrepancy can be explained by the fact that the ionization probability of a trap was estimated with the use of the average value of the electric field ($F = V/d$) in the first case and with the use of the local (depending on the coordinate) electric field obtained as an accurate solution of the Poisson equation taking into account the nonuniformity of the trapped charge in the bulk of silicon nitride in the second case.

Thus, the experiment on charge transfer in silicon nitride carried out over a wide range of electric fields and temperatures is quantitatively described by the theory of the multiphonon ionization of traps. An agreement with the experiment was obtained for the bipolar model of conductivity with the same parameters (concentration, capture cross section, and optical and thermal ionization energies) of electron and hole traps in silicon nitride.

A large discrepancy found between the thermal and optical ionization energies within the theory of multiphonon ionization is evidently due to the occurrence of a strong polaron effect in Si_3N_4. Previously, the polaron model of electron and hole traps in Si_3N_4 was discussed in [1, 17, 18]. According to this model, electrons and holes in Si_3N_4 are captured by a minimal silicon cluster, namely, a Si–Si bond. The polaron model suggests that a Si–Si bond or a silicon cluster composed of several silicon atoms is a deep center for electrons, a deep center for holes, and a recombination center. A quantum-chemical simulation of a Si–Si bond in Si_3N_4 carried out in [19] qualitatively confirms this hypothesis.

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