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Two-bands charge transport in silicon nitride due to phonon-assisted trap ionization

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The charge transport in the amorphous Si_3N_4 is studied experimentally and theoretically. We have found, that widely accepted Frenkel model of the trap ionization gives the unphysical low value of the attempt to escape factor, and the enormously high value of the electron tunnel mass. Experimental data are well described by theory of the two-bands conduction and the phonon-assisted trap ionization in Si_3N_4. © *2004 American Institute of Physics*.
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I. INTRODUCTION

The localization of electron and holes is the common property of amorphous semiconductors and dielectrics.[1] The amorphous silicon nitride SiN_x ($x \leqslant 4/3$) has a property to localize electrons and holes with the gigantic lifetime, e.g., >10 years at 300 K.[2] The memory effect in SiN_x is widely used in silicon nonvolatile memory devices.[3] The charge transport in the silicon-oxide-nitride-oxide-silicon devices with a moderate thickness of SiN_x is controlled by the charge localized in deep traps in the bulk of the SiN_x. Therefore, the current dependence on the applied voltage or temperature is determined by the corresponding dependence of the trap ionization rate. Presently, it is widely accepted that the trap ionization mechanism in SiN_x is Frenkel effect, which assumes the coulomb barrier lowering effect in the high electric field.[4,5] However, experimental data treated within this model give unphysical low attempt to escape factor such as $v \approx 10^6 - 10^9$ sec^{-1},[6,7] that is, in contrary to the original Frenkel's paper where this value was estimated as $v \approx 10^{15}$ sec^{-1}.[4] Recently, the Frenkel model was extended to low temperatures by taking into account the mechanism of the thermally assisted tunnel (TAT) trap ionization.[8] The fitting of experimental data by this extended model gives the enormously high value of the effective mass for the tunnel electron in SiN_x such as $m^* \approx 4\ m_0$.[8] This value is by one order higher than the experimental value $m^* \approx 0.3 - 0.6\ m_0$.[9,10] As it was shown in Ref. 8 this discrepancy between experiment and theory can be avoided by the assumption that in SiN_x the multiphonon trap ionization mechanism is valid.[11] In Ref. 8 experimental data of the current dependence on voltage and temperature were fairly well described within the semiclassical approach to the multiphonon trap ionization model[11] and one-band conductance. However, as it was unambiguously established,[6,7,12–15] the charge transport in SiN_x is due to simultaneous electron and hole motion and, therefore, two-bands conductance should be taken into account. The goal of present paper is the experimental study of charge transport in SiN_x for both cases of gate voltage polarities and the quantitative comparison of experiment data with the prediction of the quantum model of the phonon-assisted trap ionization in SiN_x.[16]

II. SAMPLES

As the substrate Czochralski *n*-type silicon with the resistivity of 7.5 Ω cm was used for fabrication the metal-nitride-oxide-silicon (MNOS) structures. The oxide and nitride thicknesses were determined by ellipsometty. The thin tunnel oxide with the thickness of 1.8 nm was thermally grown on silicon at 760 °C. The low pressure chemical vapor deposited silicon nitride with the thickness of 53 nm was evaporated at 760 °C. The ratio of $SiH_2Cl_2/NH_3 = 0.1$. Al electrodes with square 5×10^{-3} cm^2 were made with photolithography.

III. THEORY

Figures 1(a) and 1(b) shows energy diagram of MNOS structure for the two-bands model of the electron and hole transport in Si_3N_4 for both polarities. This model assumes the electron injection into nitride from the negatively biased contact and the hole injection from the positively biased contact.

Our model assumes the possibility of recombinations of the free electrons with localized holes and free holes with localized electrons in the case of equal recombination cross sections, i.e., $\sigma_r^e = \sigma_r^h = 5 \times 10^{-13}$ cm^2.[15] The carrier transport in nitride is described within the two-bands model of the electron and hole drift in dielectric under the applied field. The model takes into account Shockley-Read-Hall approach for the trap population, the continuity and Poisson's equation and considers the carrier double injection from the silicon substrate and from the opposite electrode (Al gate) according

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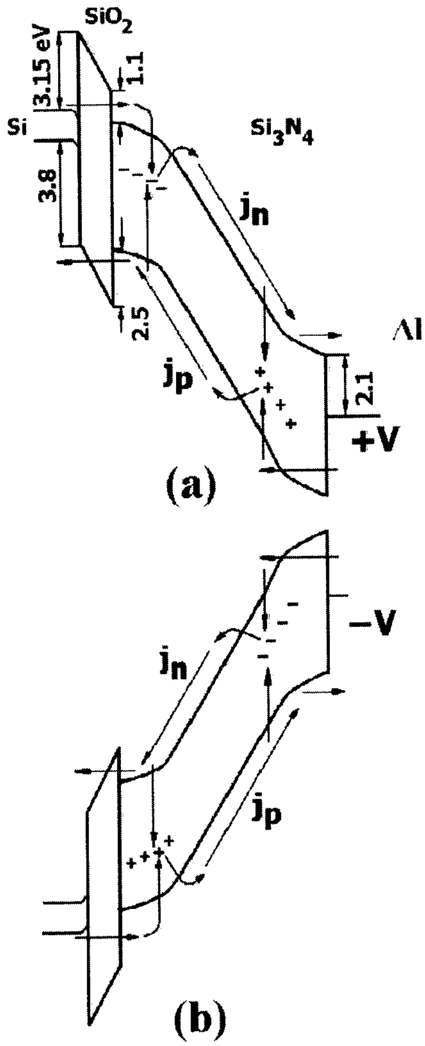

FIG. 1. Energy diagrams of MNOS structure, for two-bands model of charge transport in Si_3N_4: (a) positive potential on the metal gate, (b) negative potential on the metal gate.

to the modified Fowler-Nordheim mechanism. The system evolution is described by the following system of equations:

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

$$\frac{\partial n_t(x,t)}{\partial t} = \sigma \nu n(x,t)[N_t - n_t(x,t)] - n_t(x,t)P^{(n)}(x,t) - \sigma_r \nu p(x,t) n_t(x,t), \tag{2}$$

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

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

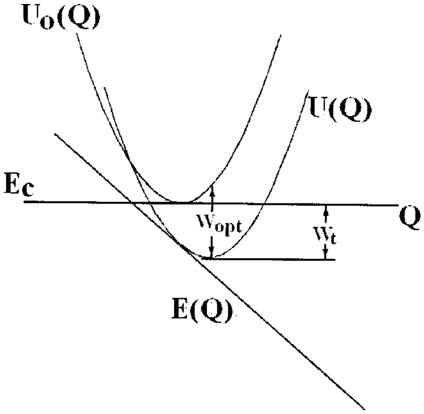

FIG. 2. Configuration diagrams for empty trap $U_0(Q)$ and filled trap $U(Q)$. $E(Q)$ is energy of bounded electron as function of normalized core coordinate Q.

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

Here n, N_t, and n_t, are densities of free electrons, electron traps, and occupied traps, respectively, p and p_t are the densities of free and captured holes. We assume the density of traps for electrons and for holes is equal. $F(x,t)$ is the local electric field, e is the electron charge, σ is the cross section of the trap, ν is the velocity of the electron or hole drift, and $\varepsilon = 7.5$ is the low frequency dielectric constant of Si_3N_4. The drift electron density and the hole current density are written as $j = en\nu$ and $j_p = -ep\nu$. $P^{(n,p)}$ is the probability of the trap ionization per second.

For the charge transport in silicon nitride the crucial point is the mechanism of trap ionization. Here we consider two models of trap ionization: modified Frenkel model including TAT and phonon-assisted trap ionization. The detail description of TAT can be found in Ref. 8, therefore, here we only briefly consider quantum model of phonon-assisted trap ionization.

Following Makkram-Ebeid and Lannoo,[16] we assume, that the empty trap is neutral and it is some "oscillator" or a "core" embedded in the nitride lattice, which can attract the electron (the electron trap) or the hole (the hole trap). Figure 2 shows the potential energy of the core or the so-called configuration diagram. In this model of the trap the core behaves as a harmonic oscillator with generalized coordinate Q and frequency ω. The trapped electron (hole) has the energy level that linearly depends on the core coordinate as

$$E = -\sqrt{2S}Q\hbar\omega + \text{const.}, \tag{6}$$

where S is the so-called Huang-Rhys coupling constant and $\hbar\omega$ is the energy of the associated phonon. Due to the linear dependence on Q in Eq. (6) the system composed of the bound carrier and core is also the harmonic oscillator with the shifted energy diagram as it is shown in Fig. 2. The trap is completely defined by the phonon energy W_{ph}, the thermal energy W_T, and the optical energy of the ionization W_{opt}, which meaning are clear from Fig. 2. In the external field this composed system can decay into the empty core and the free carrier (the ionization process) so that the sum of their energies is equal to the initial energy of the filled trap. Usually

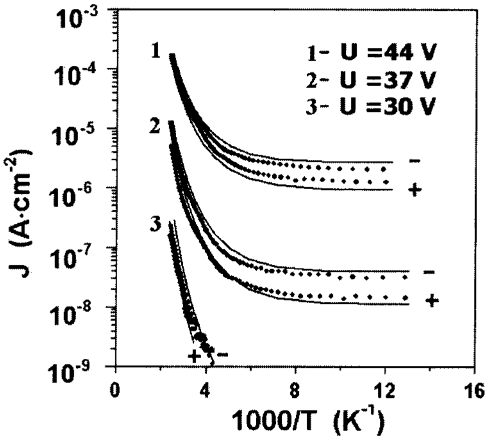

FIG. 3. Current-temperature characteristics of MNOS at different applied voltages. Experimental data are reported by dots and theoretical results are shown by solid curves. Signs (+) and (−) correspond to the positive and negative polarities of applied voltages on the gate, respectively. MNOS geometry: tunnel oxide thickness $d_{ox}=1.8$ nm, nitride thickness $d_N=53$ nm.

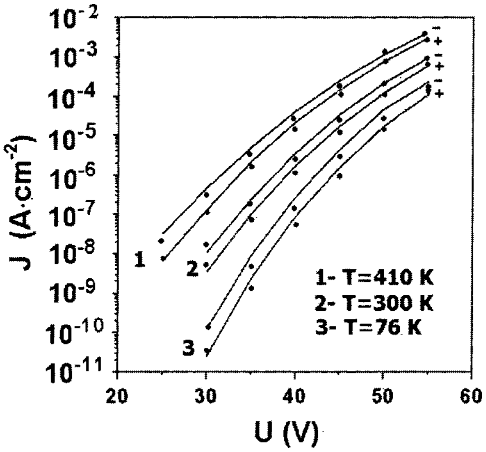

FIG. 4. Current-voltage characteristics of MNOS at different temperatures.

after the ionization process the final state of the core is an exited state and this excess of the energy the core spends to induce other lattice vibration modes. The quantum theory[16] of this kind of traps gives the following equation for the rate of the trap ionization

$$P=\sum_{n=-\infty}^{+\infty}\exp\left[\frac{nW_{\mathrm{ph}}}{2kT}-S\coth\frac{W_{\mathrm{ph}}}{2kT}\right]I_n\left(\frac{S}{\sinh(W_{\mathrm{ph}}/2kT)}\right)P_i(W_T+nW_{\mathrm{ph}}),\tag{7}$$

$$P_i(W)=\frac{eF}{2\sqrt{2m*W}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m}}{\hbar eF}W^{3/2}\right),$$

$$S=\frac{W_{\mathrm{opt}}-W_T}{W_{\mathrm{ph}}},\tag{8}$$

where I_n, is the modified Bessel function and the value $P_i(W)$ means the tunnel escape rate through the triangle barrier with the height of W.

IV. EXPERIMENT AND THEORY COMPARISON

Two sets of experiments have been performed to obtain most of the information about the trap ionization mechanism. For the first set the current dependence on temperature was measured for both bias polarities. For the second one the current as a function of applied voltage was registered.

The experimental current amplitude dependence on temperature at different fixed positive and negative voltages (on Al) is reported in Fig. 3 in Arrhenius coordinates as $J-T^{-1}$. The current is approximately constant for temperature lower than 200 K and rapidly increases with temperature at the high temperature region ($T>200$ K). The similar behavior of the current was previously observed in Refs. [5,8]. The current-voltage characteristics are reported in Fig. 4.

First we tried to fit the experimental data on the base of the modified Frenkel model including TAT. Fitting the experimental current temperature dependence in the high temperature region gives the trap energy $W=1.24$ eV. The value of attempt to escape factor determined by the absolute current adjustment is $v=10^6$ sec^{-1}. For the low temperature the fitting of the current value allows to determine the effective tunnel mass. However, to adjust the experimental current for all applied voltages we have to vary the tunnel mass within the region $m_e^*=m_h^*=4-6$ m$_0$. These mass values are one order higher than the experimentally determined tunnel mass of the electron and the hole in SiN$_x$ 0.3–0.6 m$_0$.[9,10] So, we can conclude that Frenkel model formally describes the electron and hole transport in SiN$_x$, but leads to the unphysical low attempt to escape factor, and the enormously large value of the effective tunnel mass.

To fit the experimental data by model of the phonon-assisted trap ionization the varied parameters were W_{opt}, W_T, W_{ph} for the fixed values of the tunnel effective masses $m_e^*=m_h^*=0.5m_0$. The procedure of the fitting was very similar to those described Ref. 16. As the result we obtain the following trap parameters: $W_{\mathrm{opt}}=2.8$ eV, $W_T=1.4$ eV, $W_{\mathrm{ph}}=60$ meV. These values are little bit less than those found in Ref. 8, because of which we use the two-bands conduction and the quantum model of the phonon-assisted trap ionization instead of one-band conduction and the semiclassical approximation for the phonon-assisted trap ionization.[8]

The experimental current magnitude at the negative potential polarity on the metal is about three times larger, than one at the same voltage but for positive potential on metal. This feature is reproduced in simulations. The explanation is that for the negative polarity the main channel for the charge injection in nitride is the hole injection and for the positive polarity is the electron injection through Si/SiO$_2$ interface. As one can see from the energy diagrams, Fig. 1, the effective barrier for the hole is lower than one for the electron on Si/SiN$_x$ interface. Hence, one can expect that the hole injection should be larger than the electron one for the same magnitude of the field in bottom oxide.

The best agreement between experimental *I-V-T* data and theoretical calculations was obtained for identical parameters of electron and hole traps such as densities, cross sections, optical energies, thermal energies, and tunnel effective masses. Previously this assumption was made to explain the experimental results[6] that show the identical behavior of hole or electron retentions from nitride under different applied pull voltages. Also this hypothesis is supported by the relatively week dependence of the current from the polarity in MNOS structures.[12]

The fitting of experimental data gives the optical trap energy two times larger, than the thermal trap energy $W_{\mathrm{op}} \approx 2W_T$. It means, that the activation energy for the electron and hole capture by traps is close to zero.[11] This fact agrees with the week temperature dependence of electron and hole trap cross sections SiN_x in observed in experiment.[17]

The phonon energy $W_{\mathrm{ph}}=60$ meV obtained in our simulation coincides with the phonon energy of amorphous silicon, which was determined by Raman spectroscopy.[18,19] The coincidence of the trap phonon energy with the amorphous silicon phonon energy suggests that amorphous silicon nanoclusters play role of electron and hole traps in silicon nitride. This hypothesis was previously proposed in Ref. 2. The quantum confinement in amorphous silicon quantum dots embedded in silicon nitride was observed by optical absorption and photoluminescence experiments.[20,21] Recently, it was directly demonstrated, that amorphous Si nanoclusters can capture electrons and holes in silicon nitride.[22]

V. CONCLUSION

The experimental *J-V-T* data for SiN_x formally are described by two-bands conduction and Frenkel model of the coulomb trap ionization. However, interpretation of the experiment in terms of Frenkel model leads to unphysical low attempt to escape factor, and the enormously large value of tunnel effective mass. The charge transport in silicon nitride is quantitatively described by the two-bands conduction model and the quantum model of the multiphonon mechanism of trap ionization. The best fitting of experimental data corresponds to the same values of parameters for electron and hole traps such as densities, optical, thermal energies, and phonon energies. The last coincides with phonon energy of amorphous silicon. This fact supports the assumption that the electron and hole traps in silicon nitride are amorphous silicon nanoclusters.

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