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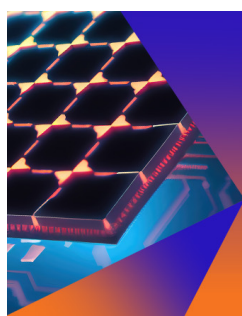
Nature of traps responsible for the memory effect in silicon nitride

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Nature of traps responsible for the memory effect in silicon nitride

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Nature of traps responsible for the memory effect in Si_3N_4 still remains the subject matter of much discussion. Based on our quantum chemical simulation results, Si–Si bonds can be identified as traps for electrons and holes with localization energies falling within the ranges of $W_t^e = 1.2 - 1.7$ eV and $W_t^h = 0.9 - 1.4$ eV. Within the multiphonon trap ionization model, our experimental data on Si_3N_4 conductivity have allowed us to evaluate the thermal ionization energies of electron and hole traps in Si_3N_4 as $W_t^e = W_t^h = 1.4$ eV. The same value of 1.4 eV was obtained as half the Stokes shift of the 2.4 eV green photoluminescence line observed in Si_3N_4 films under excitation with 5.2 eV. Thus, the data obtained in the present study strongly suggest that Si–Si bonds are responsible for localization of electrons and holes in Si_3N_4 . Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4959830>]

Silicon nitride (Si_3N_4) and silicon oxide (SiO_2) are the two key dielectrics widely used in semiconductor devices. Silicon nitride exhibits a memory effect, or the property to localize injected electrons and hole with giant charge-carrier lifetimes in localized state, about 10 years at 150 °C.¹ Such a memory effect is used in TANOS (TaN-Alumina-Nitride-Oxide-Silicon) non-volatile flash memory applications.² Also, silicon nitride is used as a memorizing medium in next-generation 3D flash memory devices.³

There have been many publications devoted to the experimental and theoretical study of the nature of traps responsible for the memory effect in Si_3N_4 . Different approaches were adopted for such traps, including their identification as nitrogen atoms,⁴ Si–H bonds,⁵ triple-coordinated silicon atoms with unpaired electron ($\equiv\text{Si}\cdot$ or K-center),^{6–8} Si–Si bonds,^{9–11} or silicon clusters.^{12,13} The capability of defects to localize (capture and retain in localized state) electrons/holes is often evaluated by allocating the static energy levels of defects within the bandgap of Si_3N_4 without any consideration given to the subsequent shift of the defect levels due to lattice relaxation.¹⁴ However, due to the polaron effect (electron–phonon interaction), a substantial shift of defect levels in the energy spectrum of dielectric material can be observed due to the redistribution of electron density and displacements of atoms in the vicinity of defects.^{15,16} Simultaneously, a large value of the Stokes shift of photoluminescence (PL) bands in Si_3N_4 is indicative of a strong polaron effect for electron/hole localization in this dielectric.¹⁷ In spite of numerous studies, the nature of defects responsible for electron/hole localization in Si_3N_4 still remains a widely debated matter. It can be assuming that the Si–Si bond is the predominant neutral defect in Si_3N_4 because of its diamagnetic defect, and Si_3N_4 films have no electron spin resonance signal. The goal of the present work was to examine the capability of Si–Si bonds to localize electrons and holes within the dielectric by giving proper consideration to the polaron effect, i.e., by matching together

the experimental and theoretical energy values of electron/hole traps in Si_3N_4 .

For photoluminescence experiments, a silicon nitride film about 100 nm thick was deposited onto a silicon substrate from a mixture of SiH_4 and NH_3 ($\text{NH}_3/\text{SiH}_4 = 50$) using a deposition process held at 800 °C. Current–voltage characteristics of $\text{Si-SiO}_2(1.8\text{ nm})\text{-Si}_3\text{N}_4(53\text{ nm})\text{-Al}$ structures were measured as described in Ref. 18. Photoluminescence was measured at room temperature as described in Ref. 19.

Simulations were performed using the Quantum-ESPRESSO software within the framework of the density functional theory (DFT) for the model of periodically arranged supercells.²⁰ The defects were calculated as occurring in $\alpha\text{-Si}_3\text{N}_4$ crystal phase, considered as the closest one to the amorphous state. Moreover, it is known that the electronic structure of defects in dielectrics is defined by the short-range order; that makes it reasonable to compare the results for amorphous Si_3N_4 with crystalline $\alpha\text{-Si}_3\text{N}_4$.²¹ For simulation of Si–Si bonds, 84 supercells with one nitrogen atom replaced with one hydrogen atom for introduction of Si–H bonds into the cells were used as it was proposed in Ref. 9. Nitrogen vacancy was considered as a defect that could occur at four non-equivalent sites of the Si_3N_4 lattice having different bond distances to neighbor silicon atoms. The energies of the electrons and holes trapped at the defect, W_t^e and W_t^h , were evaluated as

$$W_t^{e/h} = E_p^{-1/+1} + E_d^0 - E_p^0 - E_d^{-1/+1}.$$

Here, E_p^0 and E_d^0 are the values of the total energy of, respectively, a neutral ideal supercell and a defect supercell, and $E_p^{-1/+1}$ and $E_d^{-1/+1}$ are the values of the total energy of, respectively, an ideal supercell and a defect supercell with one electron having been introduced into, or removed from, the equilibrium configuration. The latter calculation method to good accuracy fits experimental data for structural parameters (bond lengths) and for the bandgap energy of silicon nitride, $E_g = 4.6$ eV.²²

The structure of Si–Si defect in Si_3N_4 is shown in Figure 1. All non-equivalent defect positions in $\alpha\text{-Si}_3\text{N}_4$ have

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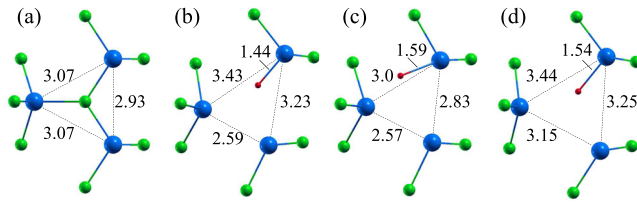


FIG. 1. Fragment of the Si₃N₄ perfect cell (a), as well as cells with the Si-Si defect in the neutral (b) negatively charged (c), and positively charged (d) states. The distances shown in angstroms. The silicon atoms are blue, nitrogen—green, and hydrogen—red.

similar behavior: a hydrogen atom is moving closer to one of the silicon atoms at a distance of 1.5 Å, while the remaining two silicon atoms come together to about 2.6 Å (original distance is 3.1 Å). The addition of an electron does not change the Si-Si bond length, but the Si-Si bond becomes noticeably closer to the third silicon atom. On the contrary, adding a hole leads to the anti-bonds of Si-Si (bond length increases by ~15%), and the distance between these atoms and the third silicon atom remains almost unchanged. The Si-H bond length increases in the localization of both electrons and holes

According to our quantum-chemical simulations, the localization of electrons and holes at Si-Si bonds within Si₃N₄ presents an energetically favorable process. Depending on the allocation of the Si-Si bond in the cell, the energy gain for electron trapping at the defect proved to be within the range $W_t^e = 1.2 - 1.7$ eV and the same gain for hole trapping, within the range of $W_t^h = 0.8 - 1.4$ eV. Thus, Si-Si bonds in silicon nitride act as amphoteric traps capable of capturing both electrons and holes.

The band diagram of a nonbiased metal-nitride-oxide-semiconductor (MNOS, Si-SiO₂-Si₃N₄-Al) structure (a) and a similar diagram of the same structure biased with a positive potential applied to the metal (b) are shown in Figure 2. Normally, such structures exhibit bipolar conductivity: under negative bias voltages applied to Al, electrons are injected into silicon nitride out of the metal while under positive bias voltages holes are injected into Si₃N₄ out of Si.¹⁸

Presently, the conductivity in Si₃N₄ is believed to be limited by trap ionization that occurs by the Frenkel mechanism.²³ Experimental current-voltage characteristics of Si₃N₄ measured in a wide range of ambient temperatures and applied electric fields can be adequately understood within the Frenkel model. However, the theory fails to provide an adequate fit of theoretical results to experimental data with

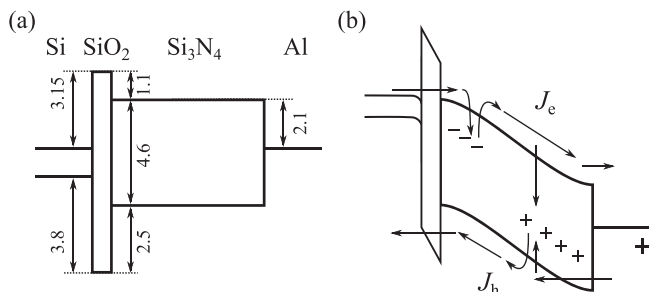


FIG. 2. The band diagram of a Si-SiO₂-Si₃N₄-Al structure under zero biasing (a) and with a positive bias applied to the metal (b).

reasonable values of involved parameters, such as the frequency factor and the tunneling effective mass of charge carriers. For instance, good matching between the model and the experiment can only be achieved on the assumption of an abnormally low value of frequency factor, $\nu \approx 10^6$ s⁻¹, whereas the frequency factor value estimated by the Frenkel model proved to be about $\nu \sim 10^{15}$ s⁻¹. Besides, the Frenkel model well fits the experimental current-voltage characteristics of Si₃N₄ only on the assumption of an abnormally large value of electron tunneling effective mass $m^* = 4m_e$, where m_e is the free electron mass. It should be noted here that the electron effective mass obtained from experiments has a lower value of $m^* = 0.5m_e$.²²

Current-voltage characteristics of Si-SiO₂-Si₃N₄-Al structures measured at different temperatures and positive biasing at the metal electrode are shown in Figure 3. In the multiphonon model, the ionization probability is given by the following expression:²⁴

$$P = \sum_{n=-\infty}^{+\infty} \exp\left(\frac{nW_{ph}}{2kT} - \frac{W_{opt} - W_t}{W_{ph}} \coth \frac{W_{ph}}{2kT}\right) \times I_n\left(\frac{W_{opt} - W_t}{W_{ph} \sinh(W_{ph}/2kT)}\right) \hat{P}_i(W_t + nW_{ph}),$$

$$\hat{P}_i(W) = \frac{eF}{2\sqrt{2m^*W}} \exp\left(-\frac{3\sqrt{2m^*}}{4\hbar eF} W^{3/2}\right).$$

Here, F is the electric field, W_t is the thermal ionization energy of the traps, W_{opt} is the optical ionization energy, W_{ph} is the phonon energy, I_n is the modified Bessel function, and $\hat{P}_i(W)$ is the probability of tunneling of charge carrier through a triangular barrier of height W . Under different temperatures, the multiphonon ionization model well describes the current-voltage characteristics of Si-SiO₂-Si₃N₄-Al structures with the following (identical) parameters of electron and hole traps: $W_t^e = W_t^h = 1.4$ eV, $W_{opt}^e = W_{opt}^h = 2.8$ eV, $W_{ph} = 0.06$ eV.

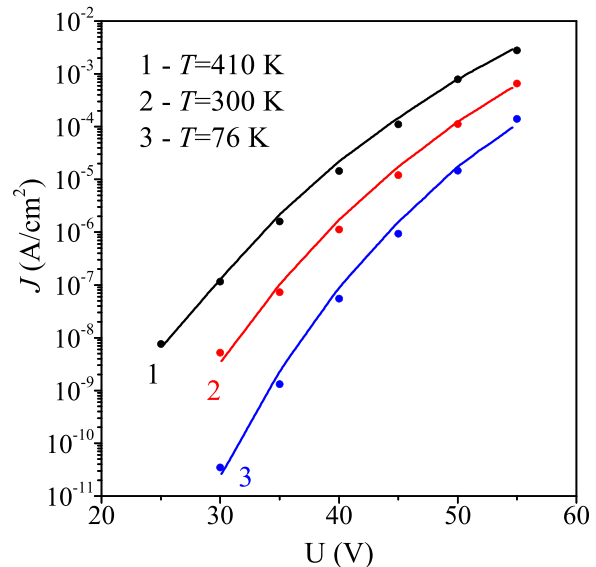


FIG. 3. Current-voltage characteristics of a positively biased MNOS structure at different temperatures. The solid line shows data calculated by the multiphonon ionization model, and the dots are experimental data.

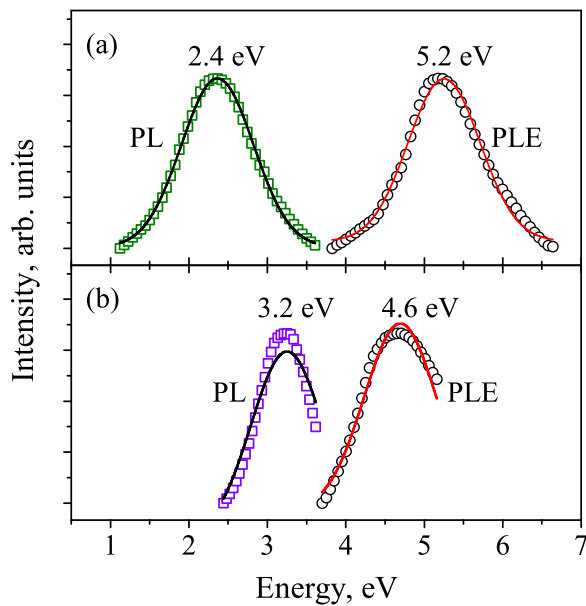


FIG. 4. The Si_3N_4 PL spectrum measured under 5.2 eV excitation and involving a 2.4 eV green luminescence line, as well as the PLE spectrum of this line (a). The Si_3N_4 PL spectrum excited with 4.6 eV and involving a 3.2 eV UV luminescence line, as well as the PLE spectrum of this line (b). Characters—experimental data; solid lines—single Gauss decompositions.

Measured photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra of Si_3N_4 films are shown in Figure 4. The excitation maximum of the green luminescence line peaking at energy 2.4 eV is at 5.2 eV. The ultraviolet luminescence band with the energy of 3.2 eV has its maximum excitation energy at 4.6 eV. The energy diagram of electronic transitions to the Si–Si bond in Si_3N_4 is shown in Figure 5(a). According to quantum-chemical modeling the level of Si–Si bond filled binding σ -orbitals is located near valence band top E_V and the unfilled antibonding σ^* -orbital level is located near the conduction band bottom E_C .^{14,25} The UV photoluminescence band at the energy of 4.6 eV corresponds to the electron transition from the binding σ -orbital to σ^* antibonding orbital of the Si–Si bond. The multiphoton transition of an electron from a binding σ -orbital to the localized state corresponds to the capture on the trap with energy 1.4 eV. The subsequent electron transition from a localized state to the unfilled binding σ -orbital corresponds to a radiative transition with energy 3.2 eV. On the other hand, a hole from bonding σ -orbital transits to the localized state with the energy of 1.4 eV, and the electron

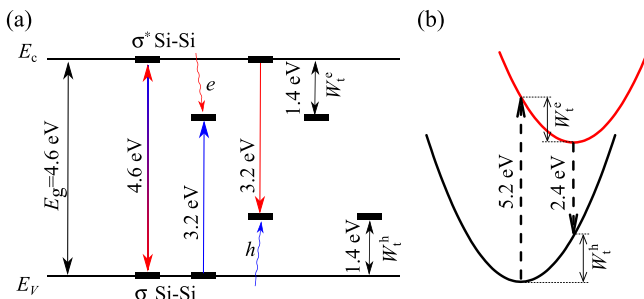


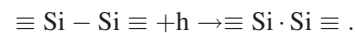
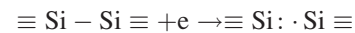
FIG. 5. (a) The energy diagram of electronic transitions in the Si–Si bond in Si_3N_4 associated with the UV PL. (b) A configuration diagram of the optical transitions related to the 2.4 eV green photoluminescence line in Si_3N_4 .

from the antibonding σ^* -orbital transits to the unfilled state with quant energy radiation 3.2 eV. Thus, in our model, the transition with energy 3.2 eV is the result of radiative recombination of localized electron with a hole and a localized hole with an electron. The energy difference $4.6 - 3.2 = 1.4$ eV coincides with electron and hole traps energy $W_t^e = W_t^h = 1.4$ eV.

A configuration diagram illustrating the optical transitions associated with the green photoluminescence line is given in Figure 5(b). A vertical Frank–Condon transition from the occupied ground state to the excited empty state corresponds to the luminescence excitation maximum observed at energy 5.2 eV. From this state, the defect goes into the excited-state energy minimum by emitting phonons, with the reduction of its electron energy being equal to the polaron energy of 1.4 eV. Subsequent vertical Frank–Condon transition from the excited-state minimum into the non-relaxed ground state corresponds to an optical transition with the energy of 2.4 eV. Further relaxation of the defect accompanied with phonon emission yields a polaron with electron/hole trapping energies of 1.4 eV. The polaron energies coincide with thermal trap ionization energies. The latter suggests that it is Si–Si bonds that act as electron and hole traps in silicon nitride.

Our quantum-chemical simulations confirm that Si–Si bonds in Si_3N_4 present amphoteric traps that can capture both electrons and holes. A comparison of the value of half the Stokes shift for the green photoluminescence line, $W_t = (5.2 - 2.4)/2 = 1.4$ eV, with the electron/hole trap energies, $W_t^e = W_t^h = 1.4$ eV, suggests that the 2.4 eV green photoluminescence line and its 5.2 eV excitation maximum refer to optical ionization of the Si–Si defect. The calculated energy is in a good agreement with electron/hole trapping energies that fit experimental data within experimental inaccuracy.

The neutral diamagnetic Si–Si bond with trapped electron or hole passes into paramagnetic state by the following schemes:



Previously, it was shown experimentally that silicon nitride with localized electrons/holes exhibits no paramagnetic resonance signal.^{26–28} In Refs. 27 and 29, a ferromagnetic pairing model for electrons localized at deep neutral traps in Si_3N_4 was proposed. A dielectric with a high density of randomly occurring deep neutral traps was considered. Due to the Coulomb repulsion of electrons localized at traps, the density of traps filled with electrons proved to be significantly lower than the total trap density. According to this model, resonant tunneling of localized electrons through empty traps leads to antiferromagnetic electron pairing. The latter model provides a reasonable explanation to the experimentally observed absence of paramagnetic resonance due to trapped electrons/holes in amorphous silicon nitride.

In conclusion, in the present paper, we study the electronic structure of Si–Si bonds defect in silicon nitride by means of charge transport and photoluminescence experiments and quantum-chemical simulation. Half the Stokes shift of the 2.4 eV green photoluminescence band is observed

in Si₃N₄ films under excitation with 5.2 eV is 1.4 eV. This value coincides with the electron and hole traps energy $W_t^e = W_t^h = 1.4$ eV that were found from the charge transport experiments. The energy difference of the UV photoluminescence peak at 3.2 eV and the maximum of the excitation spectrum of this band at 4.6 eV also coincides with the traps energy. The DFT simulation indicates that the neutral Si–Si bonds in Si₃N₄ are the amphoteric traps for electrons and holes.

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