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CONDENSED MATTER

Si–Si Bond as a Deep Trap for Electrons and Holes in Silicon Nitride

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A two-stage model of the capture of electrons and holes in traps in amorphous silicon nitride Si_3N_4 has been proposed. The electronic structure of a "Si–Si bond" intrinsic defect in Si_3N_4 has been calculated in the tight-binding approximation without fitting parameters. The properties of the Si–Si bond such as a giant cross section for capture of electrons and holes and a giant lifetime of trapped carriers have been explained. It has been shown that the Si–Si bond in the neutral state gives shallow levels near the bottom of the conduction band and the top of the valence band, which have a large cross section for capture. The capture of an electron or a hole on this bond is accompanied by the shift of shallow levels by 1.4–1.5 eV to the band gap owing to the polaron effect and a change in the localization region of valence electrons of atoms of the Si–Si bond. The calculations have been proposed with a new method for parameterizing the matrix elements of the tight-binding Hamiltonian taking into account a change in the localization region of valence electrons of an isolated atom incorporated into a solid.

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Amorphous silicon oxide (SiO_2) and silicon nitride (Si_3N_4) are two key insulators in the technology and design of silicon devices. Silicon nitride Si_3N_4 can localize electrons and holes injected into it in a localized state with a giant lifetime (10 yr at 85°C). This phenomenon is called the memory effect in Si_3N_4. Owing to the memory effect, Si_3N_4 is used as an active memory medium in flash memory devices storing information without power supply [1, 2].

The nature of traps in Si_3N_4, which are responsible for the memory effect, was studied in numerous experimental and theoretical works. The Si–H bonds [2], triply coordinated Si atoms with an unpaired electron (K-center) [3], and Si–Si bonds [4, 5] were considered as traps. The capability of defects to localize (to trap and to confine) electrons and holes is often estimated by the position of static levels of defects in the band gap of Si_3N_4 disregarding their subsequent shift [6]. However, the polaron effect (electron–phonon interaction) can significantly shift the atoms of the defect and its environment [7]. A large Stokes shift of photoluminescence in Si_3N_4 indicates a strong polaron effect at the localization of electrons and holes [7, 8]. The shift of atoms of the defect results in shifts of energy levels owing to both the polaron effect and a change in the localization region of valence electrons and, correspondingly, a change in their kinetic and potential energies.

It is currently accepted [8–12] that Si–Si bonds are responsible for the localization of charge carriers in Si_3N_4. However, such a concept faces serious contradiction. According to the quantum-chemical calculations and the experiment reported in [7], the occupied level of the bonding σ orbital of the neutral Si–Si bond is located near the top of the valence band of silicon nitride E_v. The empty level of the antibonding σ* orbital of the Si–Si bond is located near the bottom of the conduction band of silicon nitride E_c [4, 7]. Thus, the levels of bonding and antibonding orbitals are shallow. This means that the wavefunctions of shallow levels of the Si–Si bond have a large localization radius. This feature of shallow levels is responsible for giant cross sections for the capture of electrons and holes $\sigma_t^e = \sigma_t^h = 5 \times 10^{-13}$ cm^2 [8]. However, shallow levels cannot explain the giant lifetime (10 yr at 85°C) of electrons and holes in the localized state in Si_3N_4. Their giant lifetime corresponds to deep levels. Indeed, according to the experimental data, the energy levels of localized electrons and holes in Si_3N_4 are $W_t^e = W_t^h = 1.4$ eV [9].

To remove the indicated contradiction, it was hypothesized in [10] that electrons (holes) trapped in shallow states of the Si–Si bond polarize the environment, forming a potential well with a deep level in the band gap of the insulator.

The aim of this work is to theoretically analyze the capability of the Si–Si bond to create long-lived deep traps for electrons and holes in Si_3N_4 at the capture of charge carriers in shallow states.

In this work, we propose a model of two-stage formation of deep center of capture of electrons and holes. At the first stage, an electron (hole) is trapped on a shallow level near the bottom of the conduction band (top of the valence band). Such a capture is efficient because the state and, correspondingly, the capture cross section are large. At the second stage, the environment of the Si–Si bond is polarized by the trapped electron (hole) and atoms are shifted. The localization region of valence electrons in the Si–Si bond and its environment changes, leading to the shift of the level toward the band gap.

In our formulation of the problem, the calculation of the positions of the levels of the Si–Si bond in the band gap of Si_3N_4 is reduced to the calculation of the electronic structure of the Si–Si "molecule" incorporated in nonstoichiometric amorphous silicon nitride SiN_x in the concentration range $1.1 < x < 4/3$.

In the calculations, we used the Green's function method in the site representation and the tight-binding approximation. Amorphous silicon nitride was simulated by the Bethe lattice [11]. The matrix elements of the tight-binding Hamiltonian were self-consistently determined by the method that we previously proposed in [12]. This method does not require fitting parameters for the construction of the Hamiltonian.

The diagonal matrix elements of the tight-binding Hamiltonian of the ith site with the αth type of the wavefunction $H_{i\alpha,\, i\alpha} = E_{i\alpha}$ can be written in the form

$$E_{i\alpha} = E^0_{i\alpha} + U_{i\alpha} - T_{i\alpha} - E_{\alpha f}, \tag{1}$$

where $E^0_{i\alpha}$ is the energy of the αth state of the atom at the ith site of the lattice; the superscript 0 means the energy of a single atom; $T_{i\alpha}$ and $U_{i\alpha}$ are the change in the intra-atomic kinetic energy and the additional Coulomb repulsion, respectively, which appear because of a change in the localization region of valence electrons at the incorporation of this atom into the lattice and transfer of the charge to it; and $E_{\alpha f}$ is the electron affinity. The quantities $T_{i\alpha}$ and $U_{i\alpha}$ can be represented in the form

$$T_{i\alpha} = T^0_{i\alpha}\left(\frac{a_{i0}}{a_i}\right)^2, \quad U_{i\alpha} = U^0_{i\alpha}\left(\frac{a_{i0}}{a_i}\right). \tag{2}$$

Here, $T^0_{i\alpha} = \hbar^2/(2ma^2_{i0})$ and $U^0_{i\alpha}$ are the parameters of single atoms, a_{i0} is the standard covalent radius of the ith atom, and a_i is the ionic radius of this atom with the charge corresponding to its charge state in a solid. The electron affinity $E_{\alpha f}$ appears in Eq. (1) if the ith site is occupied by an anion. This term should be absent if this site is occupied by a cation because the silicon atom at the regular position in Si_3N_4 does not have localized states and is a cation, whereas this atom in the $(Si–Si)^-$ complex forms a localized state and behaves as an anion at the capture of an electron.

The off-diagonal matrix elements $H_{i\alpha,\, j\alpha}$ are linear combinations of the two-center parameters $V_{ll'm}$. The expressions of $H_{i\alpha,\, j\alpha}$ in terms of the two-center parameters can be found in [13]. They are lengthy and are not presented here. For the calculation, we used the expression [13]

$$V_{ll'm} = \frac{\eta_{ll'm}\hbar^2}{md^2}. \tag{3}$$

However, in contrast to [13], where the structure parameter $\eta_{ll'm}$ is fitting, we used the following expression proposed in our previous work [12]:

$$\eta_{ll'm} = \pm\sqrt{(n_l n_{l'})_m}, \tag{4}$$

where $l, l' = 0(s), 1(p), \ldots$ are the single-electron orbital quantum numbers for neighboring atomic sites, $m = 0(\sigma), 1(\pi), \ldots$ are the projections of l and l' on the line between the sites, and n_l is the occupation number of the ith atomic site by the electron with the orbital quantum number l:

$$n_l = -\frac{1}{\pi}\int_{-\infty}^{E_F} \mathrm{Im}[G_{il,il}(E)]dE. \tag{5}$$

The described method is a generalization of the tight-binding method in Harrison's formulation [13]. This generalization involves the following:

(a) The parameters $\eta_{ll'm}$ are not fitting and are self-consistently calculated by Eqs. (4) and (5).

(b) The additional terms $U_{i\alpha}$, $T_{i\alpha}$, and $E_{\alpha f}$, which are due to a change in the localization region of valence electrons [11–13], are self-consistently introduced in the diagonal matrix elements.

The effect of local changes in the interatomic distances and in the electron density (electron charges) on the diagonal and off-diagonal matrix elements of the tight-binding Hamiltonian can be easily included in Eqs. (1)–(5). The changed two-center parameter $V'_{ll'm}$ can be expressed in terms of $V_{ll'm}$:

$$V'_{ll'm} = V_{llm}\frac{1 + \delta\eta_{ll'm}/\eta_{ll'm}}{(1 + \delta d/d)^2}. \tag{6}$$

Formulas (4) and (6) make it possible to take into account change in the local parameters, which is due to change in both the interatomic distance δd and the local charge.

Since the calculation method used in this work cannot optimize the geometrical structure of the Si–Si bond, we used the results of the density functional theory calculation [14]. In particular, we used the distance between the neighboring silicon atoms for the optimized geometry of a nitrogen vacancy.

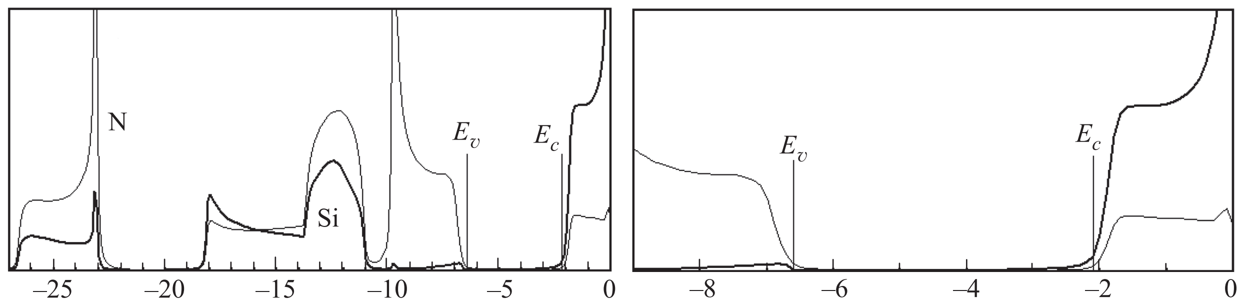

Fig. 1. Local densities of states on atoms in SiN_x ($x = 1.32$).

Fig. 2. Local densities of states on atoms of the Si–Si bond in SiN_x at $x = 1.32$.

Figure 1 shows the calculated local densities of states on (thick lines) Si and (thin lines) N atoms in Si_3N_4 (SiN_x at $x = 1.32$) in the homogeneous effective medium in the energy ranges of (left panel) –30 to 0 eV and (right panel) –9 to 0 eV. Zero energy corresponds to the vacuum level. The calculated band gap E_g =

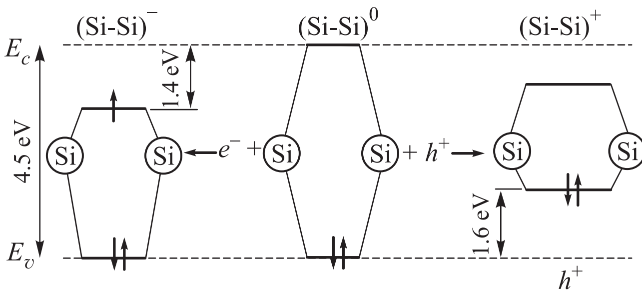

Fig. 3. Scheme of the energy levels at which electrons and holes are trapped by the Si–Si bond diamagnetic complex in SiN_x.

4.6 eV and the calculated electron affinity $\chi = 2.0$ eV are in good agreement with the experimental data [7].

The calculated local densities of states on the atoms of the Si–Si bond depending on its charge state, as well as on the neighboring nitrogen atoms, are shown in Fig. 2. The top left panel in Fig. 2 shows the scheme of the Si–Si bond with the surrounding nitrogen atoms. The numbers indicate hybrid sp^3 orbitals of silicon. The top right panel in Fig. 2 shows the types of curves demonstrating the results of the calculation of local densities of states. The thin line corresponds to the local densities of states on nitrogen atoms neighboring silicon atoms of the Si–Si bond. The other left and right panels show the results of the calculation for the energy ranges of –30 to 0 eV and –9 to 0 eV, respectively. Zero energy corresponds to the vacuum level. The second panels from the top show the calculated electronic structure of the neutral Si–Si bond denoted as $(Si–Si)^0$. The local density of states near the top of the valence band and the bottom of the conduction band has pronounced features corresponding to shallow trapping levels. The third and fourth levels from the top show the local densities of states of the atoms of the Si–Si bond with a hole, $(Si–Si)^+$, or an electron, $(Si–Si)^-$, localized on it.

Figure 3 shows the scheme of levels for the capture of electrons and holes depending on the charge at the Si–Si bond.

The reported calculations of the electronic structure of the Si–Si bond in different charge states indicate that

(a) the $(Si–Si)^-$ state with the energy 1.4 eV below the bottom of the conduction band is formed at the capture of an electron on a shallow state of the Si–Si bond;

(b) the $(Si–Si)^+$ state with the energy 1.5 eV above the top of the valence band appears at the capture of a hole on the Si–Si bond.

These results are in good agreement with experimental data [9].

To summarize, we have consistently explained the giant cross section for the capture of electrons and holes, on one hand, and the giant lifetime of charge carriers trapped on the Si–Si bond, on the other hand. It has been shown that the Si–Si bond in the neutral state provides shallow levels near the bottom of the conduction band and the top of the valence bands, which have a large trapping cross section. The polaron effect at the capture of an electron or a hole on the Si–Si bond results in the shift of levels and in a change in the geometry of the defect and its environment. The latter circumstance leads to a change in the localization region of valence electrons of the atoms of the defect and to an additional shift of the levels of the Si–Si bond by 1.4–1.5 eV to the band gap. Thus, the two-stage model of the capture of charge carriers on the Si–Si bond confirms the responsibility of this center for long-lived states in silicon nitride.

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