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Simulation of electronic structure of Si–Si bond traps in oxide/nitride/oxide structure

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Abstract

Numerical simulation using MINDO/3 was performed to study the electronic structure of Si–Si bond traps in the silicon oxide/nitride/oxide structure. Results show that the neutral diamagnetic Si–Si bond in Si₃N₄ can capture both electrons and holes. Simulation results also suggest that the creation of charged diamagnetic defect pairs is unfavorable in Si₃N₄. Electron and hole trapping models are also proposed for the Si–Si bond. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Amorphous silicon nitride Si₃N₄ has the unique feature of localizing the injected electrons and holes with a gigantic lifetime constant (~10 years at 300 K) in localized states [1,2] and has been widely used in memory devices. The oxide nitride oxide (ONO) structure has been used in EEPROM devices. It captures electrons and holes in the Si₃N₄ layer and induces a threshold voltage shift of memory transistor. In floating gate EEPROM, the ONO structure is used as the dielectric film between the floating and control gate to reduce the electronic discharge from the floating gate. The high resistance of the ONO structure (compared with SiO₂) is due to a low leakage current. In dynamic random access memory (DRAM), the ONO structures have been widely used as the dielectric in the three-dimensional (3D) stacked and trench memory capacitors to replace the thermal SiO₂ and as inter-poly dielectric in multi-level metallization of CMOS technology. The atomic and electronic structures of defects, responsible for the memory effect of Si₃N₄, have been

studied over three decades. It was suggested that the current transport properties of Si₃N₄ are governed by the deep electron and hole traps with an energy in the range of 1.5–2.3 eV [3]. On the other hand, many defects, e.g. three-coordinated silicon atoms with different charged states, over-coordinated nitrogen atoms, Si–H bonds, silicon clusters, and Si–Si bonds, have been considered as candidates for electron and hole trappings in Si₃N₄ [1–6]. However, several properties of silicon nitride film, particularly the trapping properties of the Si–Si bond, and the contribution of electron and hole in the current conduction of Si₃N₄ in ONO structures, are still unclear. This paper aims at the study of the electronic structure of traps in Si₃N₄.

2. MINDO/3 simulation

It was estimated that the enthalpy of the SiSiN₃ tetrahedron (Si–Si bond) creation in Si₃N₄ is -2.13×10^5 J/mol, and the enthalpy of SiN₄ tetrahedron creation is -1.84×10^5 J/mol [2]. At a typical LPCVD synthesis temperature of 800°C, the probability of the Si–Si bond creation in Si₃N₄ is only one to two orders lower than that of the Si–N bond. Thus, from a thermodynamic point of view, Si–Si bonds in LPCVD Si₃N₄

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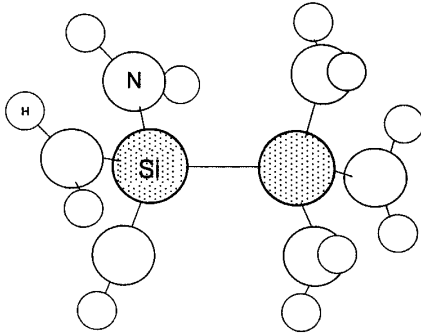


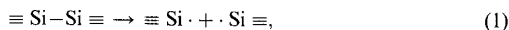
Fig. 1. Structure of $H_6N_3Si-SiN_3H_6$ cluster used for simulating the electronic structure of Si-Si bond in Si_3N_4 .

should be the intrinsic defect governing the trapping properties and charge transportation. These are several experiments supporting this conjecture [7]. In this work, we focus on the numerical simulation only.

To study the carrier capture properties of the Si-Si bonds in Si_3N_4 , numerical simulation using the modified intermediate neglect of differential overlap (MINDO) program (version 3.0) [8–10] was conducted. MINDO is a semi-empirical approximation of the self-consistent molecular-orbital theory. It is often used to calculate the geometries, spin densities, and energies of molecules and ions, as well as radicals. Fig. 1 shows the cluster structure ($H_6N_3Si-SiN_3H_6$) used in this work. The broken bonds of the boundary atoms are connected to the hydrogen atoms. The geometric relaxation of the central silicon atom pair in the Si-Si bond after the electron or hole capturing, was also considered. The values of the center parameters α and β , describing the bonds of coupling atoms for the Si-N bonds were determined by reproducing the experimental values of the bond length and dissociation energy for the SiN molecule [5]. The obtained values are: $\alpha = 1.053011$ and $\beta = 0.434749$.

3. Results and discussion

Fig. 2 shows the charge and spin variations of two silicon atoms with different Si-Si bond densities. Both charge and spin polarization are observed at distances larger than 2.3 Å and both charge and spin variations of these two silicon atoms are symmetric. Based on these observations, the following bond breaking scenario can be readily proposed.



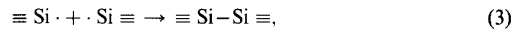
where “—” denotes a normal bond created by two electrons and “·” denotes the dangling bond (unpaired

electron). This simulation result indicates that the breaking of the neutral diamagnetic Si-Si bond should result in the creation of two neutral paramagnetic silicon atoms. The neutral paramagnetic silicon atom is coordinated with three neighbor nitrogen atoms and associated with an unpaired electron, i.e. $\equiv Si \cdot$. The simulation results do not support the following reaction,

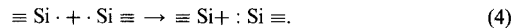


where two charged diamagnetic silicon atoms, $\equiv Si^+$ and $:Si \equiv$, can be formed.

On the other hand, when the distance between the two $\equiv Si \cdot$ defects is reduced, a neutral diamagnetic $\equiv Si-Si \equiv$ bond will be formed, i.e.



Using Anderson's defect model with a negative correlation energy, it was reported that no paramagnetism in Si_3N_4 can be found before polarization or after electron and hole localization [3, 5, 6]. This observation can be explained as follows. According to the model, interaction of two $\equiv Si \cdot$ defects results in the creation of a diamagnetic positively charged ($\equiv Si^+$) and a negatively-charged ($:Si \equiv$) defect. This process is indicated in Eq. (4).



However, MINDO/3 simulation indicates that this reaction is unfavorable in Si_3N_4 because of the large repulsive energy (~ 5 eV) of two electrons on the silicon atom. It was known that the Si-Si bond length in silicon and the Si-Si distance in Si_3N_4 are 2.35 and 3.14 Å, respectively. However, the Si-Si bond length in Si_3N_4 is unknown so far. With this connection, the energy levels for different Si-Si distances were calculated. Fig. 3 shows the calculated one-electron energy levels for the neutral Si-Si bond, where the bottom energy of the conduction band ($E_c = -2.0$) and the top energy of the valance band ($E_v = -6.5$ eV) are experimental data taken from Ref. [1].

As shown in Fig. 3, the energy level of the bonding orbital for the Si-Si bond is close to the top energy of the valance band (E_v) and the antibonding orbital level locates near the bottom of the conduction band (E_c). According to the X-ray emission and absorption spectroscopy, the energy levels of the bonding and antibonding orbitals of the Si-Si bond in Si_3N_4 should coincide with the band edges, E_v and E_c , respectively [1, 2]. An increase in the Si-Si distance leads to a shift of bonding and antibonding orbits to more negative energies, with a nearly constant gap. For quantitative correlation, a more precise and complicated model must be developed.

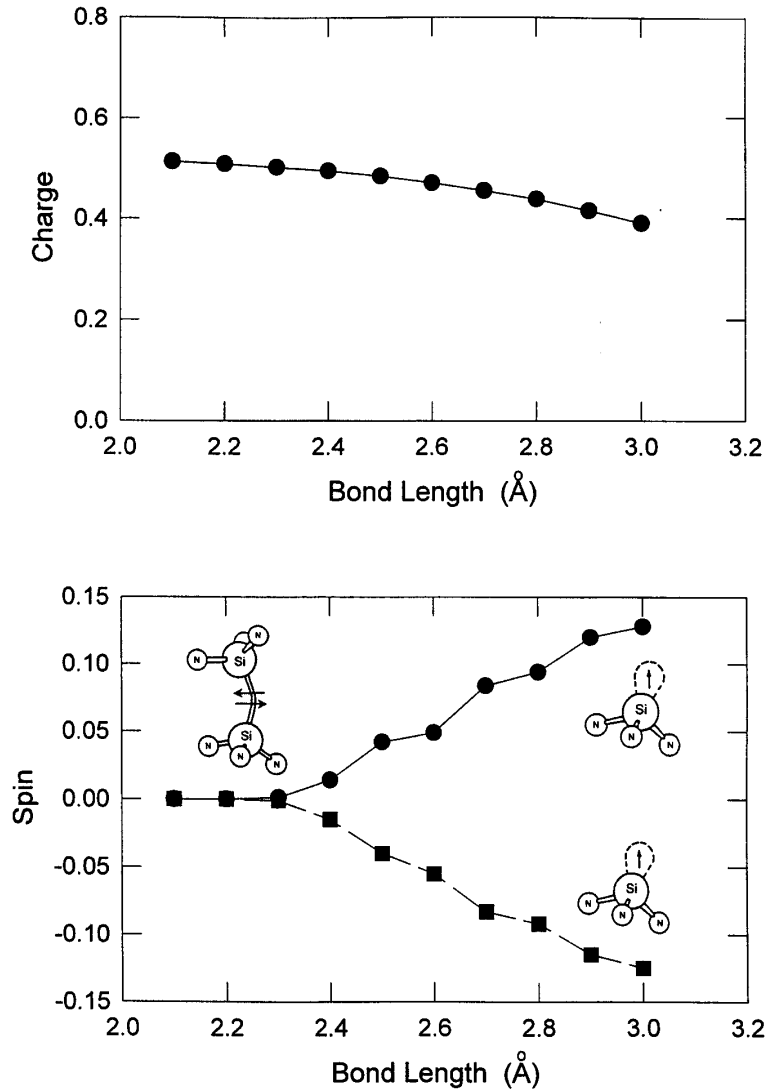


Fig. 2. Charge and spin distributions of silicon atoms for the Si-Si bond in Si_3N_4 as a function Si-Si distance.

Fig. 4 displays the charge and spin distributions of two central silicon atoms with a positively-charged Si-Si bond as a function of the initial Si-Si bond separation. Symmetric atom relaxation and symmetric distribution of the electron density for small initial Si-Si separations [Fig. 5(a)] are found. As the initial Si-Si separation increases, the atomic relaxation becomes asymmetric. At a distance larger than 2.3 Å [see the structure depicted in Fig. 5 (b) and (c)], asymmetric relaxation of the silicon atoms is observed. In particu-

lar, the Si-Si bond with a captured electron has demonstrated a significant asymmetric relaxation. The silicon atom with a high electron density moves a little ($\Delta d = 0.083$ Å) to the other silicon atom. The second positively charged silicon atom moves toward the three neighboring nitrogen atoms by 0.219 Å. This situation is similar to the E' center in SiO_2 , which is an Si-Si neutral bond with a hole trapping. Capturing of the hole on a Si-Si bond in Si_3N_4 accompanies the spin polarization, and is an active defect in electron spin

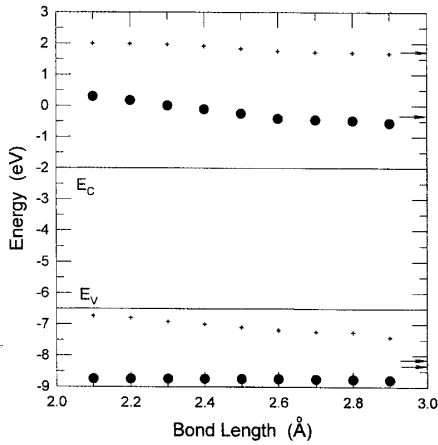


Fig. 3. Energy levels of the neutral Si-Si defect in Si_3N_4 close to the band gap for the 20-atomic cluster as a function of initial Si-Si distance. The arrows in the right hand side mark the energy levels for the N_3Si -defect in the 10-atomic cluster. The short lines mark the energy levels for cluster with Si-Si-H fragment.

resonance (ESR) measurement. The neutral silicon atom with an unpaired electron coordinated with three nitrogen atoms (N_3Si) is the well-known paramagnetic K-center in Si_3N_4 [6].

A similar simulation for the Si-Si bond with captured electron was also conducted and the results are shown in Fig. 6. For an Si-Si distance between 2.2 to 4.0 Å, the capturing of electron accompanies a symmetric Si-Si bond relaxation, and both silicon atoms shift to the nitrogen-atom side. These cluster structures are shown in Fig. 5(a) and (b). The charge and spin distributions for both silicon atoms are symmetric in that case. However, capturing of the electron on the Si-Si bond does not give rise to any spin polarization. In addition, only those Si-Si bonds with a distance of larger than 4.0 Å have spin and charge polarization.

The delocalization energies of electrons and holes were calculated using the total cluster energies estimated from Koopman's theorem. The energy for hole (E^h) and electron (E^e) delocalization from the Si-Si bond can be approximated by Eqs. (5) and (6), respectively.

$$E^h = (E_d^0 + E_b^+) - (E_d^+ + E_b^0), \quad (5)$$

$$E^e = (E_d^0 + E_b^-) - (E_d^- + E_b^0), \quad (6)$$

where E_b and E_d are the total energies of bulk Si_3N_4 cluster and cluster with $\text{H}_6\text{N}_3\text{Si-SiN}_3\text{H}_6$ which has been used for simulating the Si-Si defect in Si_3N_4 . The upper "h" and "e" indices represent hole and electron

being captured in the cluster, respectively. A total of 484 clusters composed by Si, N and H were used in the simulation, and the simulation results are considered as bulk properties of Si_3N_4 . Table 1 presents the electron and hole delocalization energies, calculated using Eqs. (5) and (6), and also the delocalization energy of the silicon dangling bond which is calculated using the $\text{H}_6\text{N}_3\text{Si}$ clusters.

The MINDO/3 simulation shows that the Si-Si bonds in Si_3N_4 can capture both electrons and holes. However, since the atom number of cluster being used for the Si-Si bond simulation is rather small when compared with the real case, the delocalization energies obtained from the simulation are not accurate enough. Hence, only qualitative remarks can be drawn here. The simulation data listed in Table 1 suggest that the broken silicon bond ($\equiv\text{Si}\cdot$) can capture the electron only; namely, the capturing of the hole in a $\equiv\text{Si}\cdot$ defect is unfavorable in Si_3N_4 . On the other hand, Si-Si bonds in Si_3N_4 can capture both electrons and holes. Fig. 7 shows the configuration coordinate diagram of the proposed defects in Si_3N_4 according to MINDO/3 simulation results. The neutral state silicon atom (middle) with an unpaired electron is more favorable than the state with negative correlation energy (charged diamagnetic atom, top diagram), and the most favorable state is the creation of the $\equiv\text{Si-Si}\equiv$ neutral diamagnetic defect (bottom). Thus, the capturing of the hole by the Si-Si bond must result in a paramagnetic center. To verify these models, electron spin resonance (ESR) measurements have been conducted previously. Only two ESR signals, corresponding to the holes being captured on Si-Si bonds in SiO_2 and three-coordinated silicon atom with an unpaired electron (Si_3Si) were observed experimentally in the SONO structures [11,12]. No signal relating to the N_3Si -defect ($g = 2.003$) is observed. To explain the absence of the ESR signal related to N_3Si in Si_3N_4 , two new effects have been proposed: (1) creation of Wigner quasi-crystal of localized holes (electrons) due to Coulomb repulsive force; and (2) antiferromagnetic ordering of localized carriers due to resonance tunneling of localized spins [13]. These models suggested that the traps for electrons and holes are due to neutral diamagnetic Si-Si bonds and the concentration of Si-Si bonds in Si_3N_4 is in the order of 10^{21} cm^{-3} [14]. Numerical estimation shows that the Zeeman splitting in Si_3N_4 is in the same order as resonance exchange energy. Fig. 8 displays the atomic model of electron and hole captured by the Si-Si bond in Si_3N_4 . According to the model, the neutral diamagnetic Si-Si bonds can capture both electrons and holes.

The "sign of carrier" in Si_3N_4 has been disputed for a long time. The conduction in Si_3N_4 is governed by the nature of electron and hole traps in Si_3N_4 . Present simulation results have shown that the Si-Si bond can

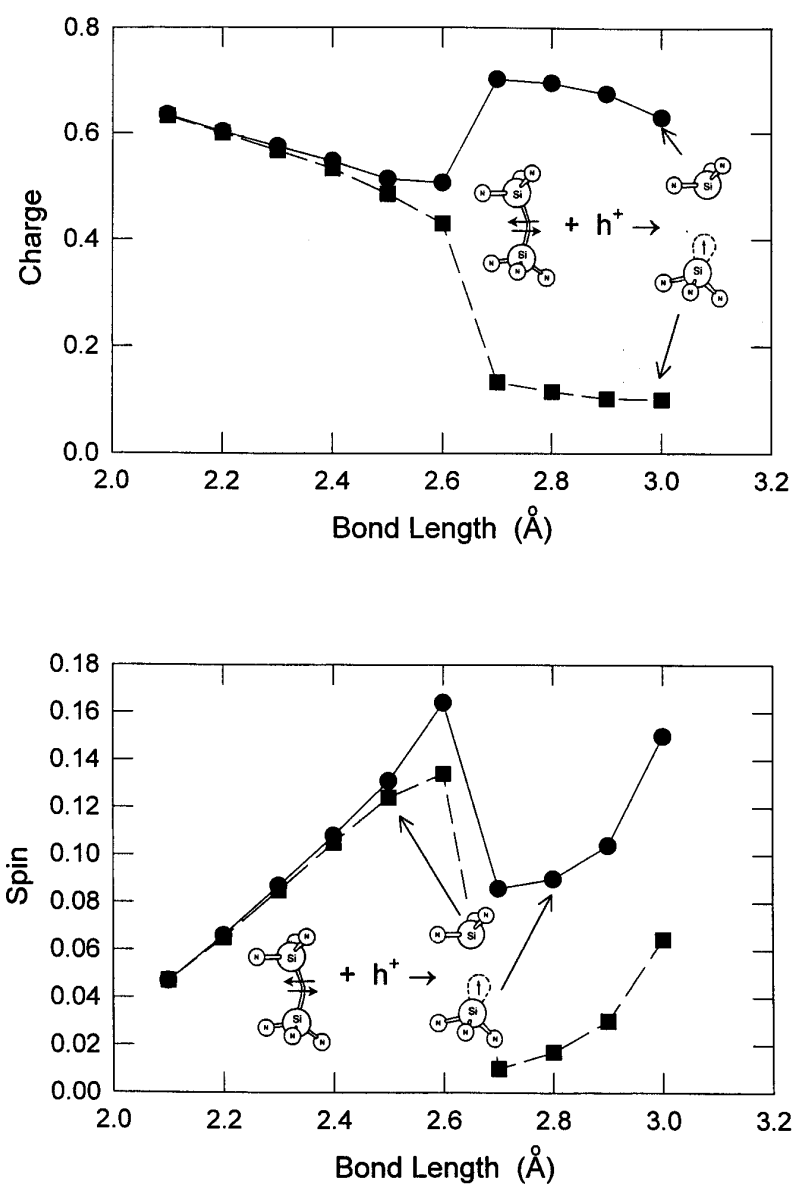


Fig. 4. Charge and spin variations of two silicon atoms of the Si-Si bond with a captured hole ($q = +1$) in Si_3N_4 .

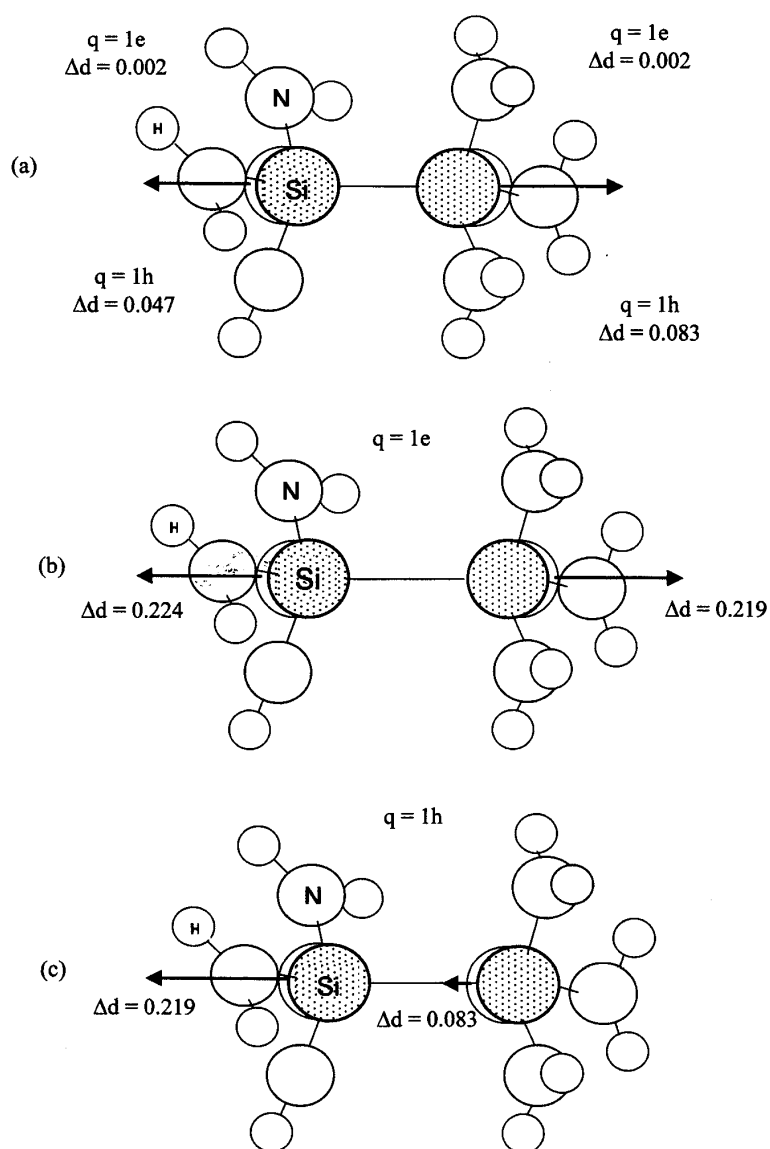


Fig. 5. Displacement of silicon atoms in $H_6N_3Si-SiN_3H_6$ cluster with (a) electron capturing and initial Si-Si distance of 2.35 Å; (b) electron capturing and initial Si-Si distance of 3.0 Å; and (c) hole capturing and initial Si-Si distance of 3.0 Å. Shaded circles represent the original locations of silicon atoms and the circles behind are the locations after displacement. The silicon atom displacement, Δd , is measured in angstroms.

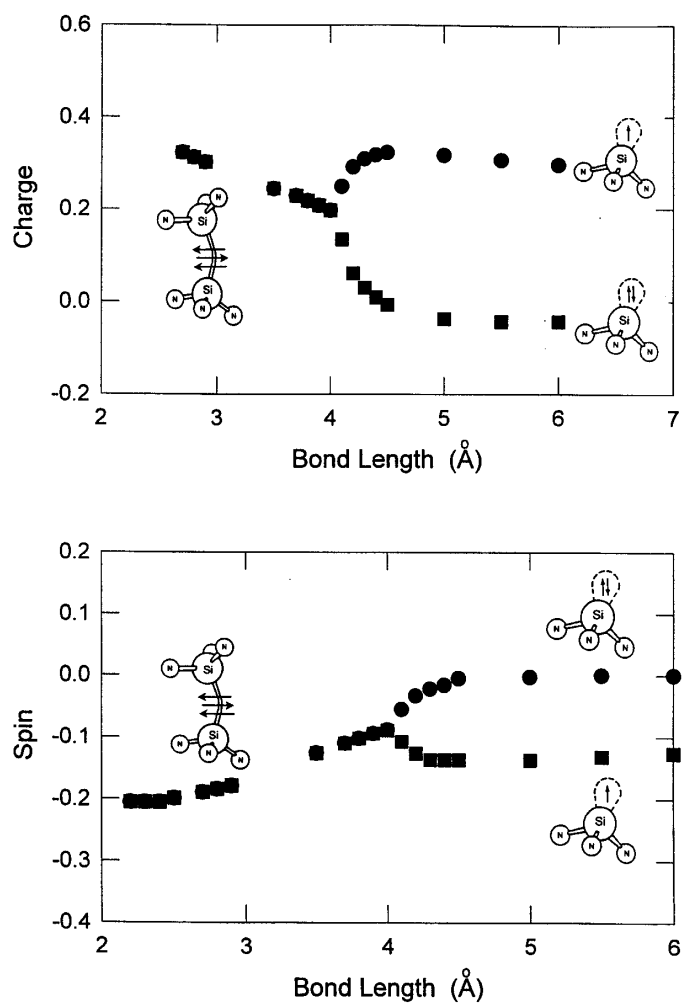


Fig. 6. Charge and spin variations of silicon atom pair for the Si-Si bond with a captured electron ($q = -1$) in Si_3N_4 .

Table 1

Electron and hole delocalization energies in the Si-Si bond and $\equiv\text{Si}\cdot$ defect in Si_3N_4 calculated using Koopman theorem

Bond/defect	Electron delocalization energy (eV)	Hole delocalization energy (eV)
$d_{\text{Si-Si}} = 2.3 \text{ \AA}$	0.3540	0.1956
$d_{\text{Si-Si}} = 3.0 \text{ \AA}$	0.8138	0.2922
$\equiv\text{Si}\cdot$	0.1650	-0.9531

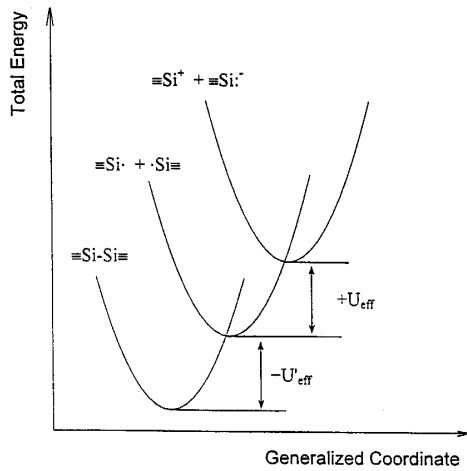


Fig. 7. Configuration coordinate diagram of three different states of the silicon atom pair in Si_3N_4 .

capture both electron and hole. The Si-Si bond contributes to the trap-assisted tunneling of charge carriers. In addition, the experiment [2] showed that the trap cross-sections for electron and hole in Si_3N_4 are almost equal, and can be as large as $5 \times 10^{-13} \text{ cm}^2$. It is also reported that the electron-hole recombination cross-section is also large and is about $5 \times 10^{-14} \text{ cm}^2$. Thus the barriers for carrier injection is the dominant factor governing the charge transport in Si_3N_4 films. According to photoemission studies [14], the electron and hole barriers in Si_3N_4 are almost the same. We are inclined to believe that the conduction in Si_3N_4 is two-band in general.

4. Conclusion

Numerical simulation using MINDO/3 has been carried out to study the electronic structure of Si-Si bond related traps in the oxide/nitride/oxide structure. Results show that the Si-Si bond, being able to trap both electron and hole, is one of the major defects in Si_3N_4 . Results also suggest that the creation of charged diamagnetic defect pairs in Si_3N_4 (with negative correlation energy) is unfavorable when compared with the creation of the neutral diamagnetic $\equiv\text{Si-Si}\equiv$ bond. The contribution of dielectric traps in current conduction in Si_3N_4 film is also discussed.

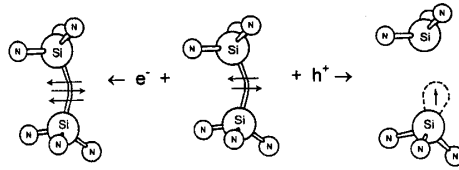


Fig. 8. Atomic model of amphoteric neutral diamagnetic Si-Si defect with electron and hole capturing in Si_3N_4 .

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