Atomic and Electronic Structures of N-Incorporated Si Oxides

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We present first-principles total-energy calculations on the N-incorporated Si oxides, regarded as a replacement for conventional SiO_2 in device technology. We investigate the energetics, charge states, and electronic structures for various bond configurations around N. While they remain in the N-incorporated structures, the charge trap states, responsible for leakage current in SiO_2, are effectively removed from the energy gap in the H-terminated structures. This shows that improvement in the electrical reliabilities of Si oxynitride films is originated not from N incorporation itself, but from the *coexistence* of N and H.

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Leakage current as well as dopant diffusion across the ultrathin gate dielectrics is one of the major problems in miniaturization of metal-oxide-semiconductor devices. The Si oxide films with N incorporation [1–13] are believed to be candidates for replacing the conventional Si oxides because they show better performances than the conventional oxides. It is indeed reported that the N-incorporated Si oxide films reduce leakage current [8], increase charge-to-breakdown value [9], and suppress boron diffusion [10]. Although it is argued that the electrical improvement is related to lower concentration of charge traps in the Si oxynitride films, the underlying physical origins remain unknown.

The charge trap is a principal cause for stress-induced leakage current (SILC) in oxide films [14]. In the conventional oxides, O vacancies [15,16] and H bridges at the O vacancies [17] are proposed to be such charge trap centers. It is thus important to identify the charge traps and their variances upon N incorporation in the Si oxynitride films.

In this Letter, we explore a variety of bond configurations around N in SiO_2 using a first-principles total-energy method. We map out the energetics, charge states, and electronic structures for the total-energy optimized atomic configurations. We found that N incorporation does not guarantee the improvement in electrical reliabilities of the Si oxynitride films since the dangling bonds (DB) or lone pairs (LP) of the N, O, and Si atoms become charge trap centers. By formation of strong bonds with H, on the other hand, the charge trap states originating from the DBs of the N, O, and Si atoms are removed from the energy gap. The presence of only H atoms, however, does not prevent charge trap generation in SiO_2 [17,18]. Therefore, the *coexistence* of N and H is crucial for better electrical properties of Si oxynitrides.

The density-functional theory (DFT) is used within the generalized-gradient approximation (GGA) [19]. The inclusion of spin degrees of freedom is important in the structures without H, where the energy gain due to spin polarization is found to be ~0.3–0.7 eV. The nuclear potentials are simulated by ultrasoft pseudopotentials for O and N [20] and norm-conserving pseudopotentials for Si and H [21]. The cutoff energy of the plane-wave basis is 25 Ry [22]. The supercell with 54 atomic sites possesses a triclinic symmetry and a special k-point is used for integration in the Brillouin zone [16]. Geometries are optimized for all atoms until the remaining force on each atom is less than 5 mRy/Å. The above parameters give the relative energetics and formation energies of O vacancies in α quartz that agree, within ±0.1 eV, with the norm-conserving pseudopotential calculation [16]. For the charged states, the compensating background charges are introduced to keep the charge neutrality in the supercell. Using a monopole model [17], we include the correction for the total energy lowering due to the spurious Coulomb interaction between the background charge and the defect charge: 0.5 and 2.1 eV for single- and double-charge states, respectively.

The bond configurations around N atoms in SiO_2 are, despite intensive studies, not well identified because they show variances according to nitridation processes or reaction gases. We thus consider a variety of possible atomic configurations containing N atoms in the network of α quartz (Fig. 1): In the S_2 structure, a N atom substitutes for an O atom and then is bonded to two Si atoms (twofold N). In the S_3 structure, the central Si moves leftward to form a threefold N atom, sacrificing the bond with its right O atom. The V_2 structure is the same as the S_2 structure, except for the Si-Si dimer formation due to an O vacancy. In the V_3 structure, the threefold N is formed by breaking the Si-Si dimer bond of the V_2 structure. In the $S_{2\mathrm{O}}$ structure, an O atom is added to the S_2 structure and a N-O bond is formed.

We then investigate the stability of the N-incorporated structures with respect to the SiO_2 matrix. We consider the reaction, $\mathrm{NO} + X \rightarrow z\mathrm{O}_2 + Y$, where X represents SiO_2 (perfect α-quartz crystal) or V_O (the α quartz with an O vacancy). Y represents S_2, S_3, or $S_{2\mathrm{O}}$ when $X = \mathrm{SiO}_2$, and V_2 or V_3 when $X = V_\mathrm{O}$. The coefficient z is 1, except for $z = 1/2$ when $Y = S_{2\mathrm{O}}$. We choose the NO molecule since it is now widely used in oxynitridation of Si or is produced by dissociation of N_2O that is also another widely used reaction gas [23]. All the reactions are endothermic with reaction energies of 3.3, 4.4, 3.2, 2.8, and 2.1 eV for $Y = S_2$, S_3, V_2, V_3, and $S_{2\mathrm{O}}$ [24], respectively, assuming

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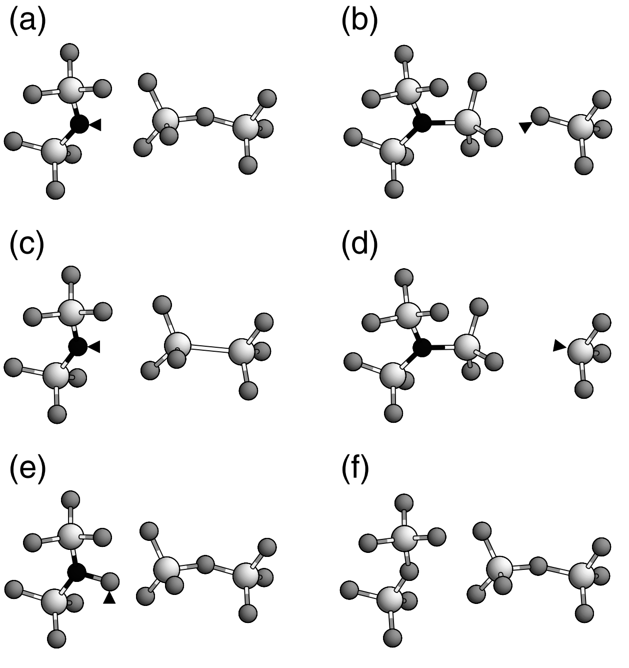

FIG. 1. Structural models for N incorporation in α quartz: (a) S_2, (b) S_3, (c) V_2, (d) V_3, (e) $S_{2\mathrm{O}}$, and (f) α quartz as a reference. Lightly grayed, darkly grayed, and black balls indicate Si, O, and N atoms, respectively. See the text for detailed explanation for structures. The arrowheads in panels (a)–(e) indicate the atoms that are bonded to a H atom in the corresponding H-terminated structures, labeled as $S_{2\mathrm{H}}$, $S_{3\mathrm{H}}$, $V_{2\mathrm{H}}$, $V_{3\mathrm{H}}$, and $S_{2\mathrm{OH}}$, respectively.

that both the reactant (NO) and product (O_2) gas molecules stay in the oxide film. We further consider other reactions for $X = V_{\mathrm{O}}$; i.e., $Y = S_{2\mathrm{O}}$ with $z = 0$, and $Y = S_2$ with $z = 1/2$. It is found that they are exothermic with reaction energies 4.8 and 3.6 eV, respectively. These results indicate that the N substitution for O in SiO_2 is unlikely even near the O vacancy, while the O vacancy itself is easily annihilated by N. Even if we consider the exothermic reactions in the latter, the N incorporation is thermodynamically limited in SiO_2, since the concentration of the O vacancy is low, 10^{18} cm^{-3} at most [16,25]. This finding is consistent with most experiments reporting only a few atomic percent of N concentration in Si oxynitrides. After the reactions, relative stability of the five structures is assessed by comparing the formation energies as a function of the oxygen chemical potential μ_{O}. For a wide range of physically relevant μ_{O}, the formation energy of $S_{2\mathrm{O}}$ is higher than those of the other four structures by more than 3 eV.

Chemically active DBs are likely in the five structures that we have examined above. (arrowheads in Fig. 1). Hence, we further consider the H-terminated counterparts of the five structures, labeled as $S_{2\mathrm{H}}$, $S_{3\mathrm{H}}$, $V_{2\mathrm{H}}$, $V_{3\mathrm{H}}$, and $S_{2\mathrm{OH}}$, respectively. The H termination would take place readily, since H is ubiquitous and diffuses very fast in SiO_2 with a barrier of 0.22 eV [26]. In this way, the present models include local arrangements experimentally observed: The most dominant $\mathrm{N{\equiv}Si_3}$ species (in S_3, V_3, $S_{3\mathrm{H}}$, and $V_{3\mathrm{H}}$) and the minor species such as $\mathrm{N{=}Si_2}$ (in S_2 and V_2) [4,6,7], $\mathrm{O{-}N{=}Si_2}$ (in $S_{2\mathrm{O}}$) [4–6], $\mathrm{H{-}N{=}Si_2}$ (in $S_{2\mathrm{H}}$ and $V_{2\mathrm{H}}$) [11], and $\mathrm{HO{-}N{=}Si_2}$ (in $S_{2\mathrm{OH}}$).

The atomic bond lengths are sensitive to the local bonding configurations. The Si-N bond lengths for the twofold N atoms (S_2 and V_2) are about 1.68 Å. They increase to 1.75 ± 0.02 Å for the threefold N atoms (S_3 and V_3), in agreement with previous calculations [12,27]. The bond angles around the threefold N atoms are 120.0° ± 3.0°, which means that the N atom and its surrounding Si atoms lie nearly in the same plane. Upon H termination, most bond lengths change little, except for the N-O bond in the $S_{2\mathrm{OH}}$ structure whose length increases from 1.32 to 1.44 Å [28].

The stability among different charge states in their equilibria is obtained by comparing $\Omega(Q,\mu) \equiv E(Q) + Q\mu$, where $E(Q)$ is the total energy of the charge state Q, and μ is the electron chemical potential, i.e., the Fermi level in the energy gap. Figure 2 shows $\Omega(Q,\mu)$ for the N-incorporated structures as a function of μ for the doubly positive ($++$; $Q = 2$), positive ($+$; $Q = 1$), neutral (0; $Q = 0$), and negative ($-$; $Q = -1$) charge states. The μ value, $\mu_{\mathrm{th}}(Q/Q+1)$, at which $\Omega(Q,\mu) = \Omega(Q+1,\mu)$, determines the relative stability of the Q and $(Q+1)$ charge states. The μ_{th} values, also called

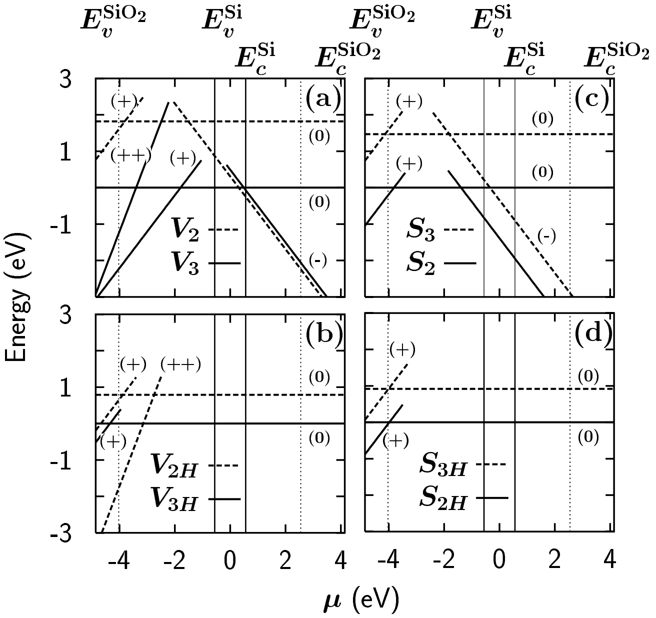

FIG. 2. Relative formation energies $\Omega(Q,\mu)$ of the N-incorporated structures as a function of the electron chemical potential μ in the energy gap of α quartz: (a) V_2 and V_3, (b) $V_{2\mathrm{H}}$ and $V_{3\mathrm{H}}$, (c) S_2 and S_3, and (d) $S_{2\mathrm{H}}$ and $S_{3\mathrm{H}}$. The energies for the doubly positive ($++$), positive ($+$), neutral (0), and negative ($-$) charge states are shown. The zero is the middle of the Si energy gap, and both ends of μ in each panel are the experimental valence band maximum (VBM) and conduction band minimum (CBM) of α quartz ($E_v^{\mathrm{SiO_2}}$ and $E_c^{\mathrm{SiO_2}}$), respectively. The VBM and CBM of bulk Si (E_v^{Si} and E_c^{Si}) are represented by vertical lines. The density-functional VBM and CBM of α quartz are shown as a reference by vertical dotted lines near both ends of μ.

TABLE I. Thermodynamic levels μ_{th} for the N-incorporated structures. Values are with respect to the middle of the Si gap, calibrated to be 4.9 eV above the experimental VBM of $\mathrm{SiO_2}$.

Configuration	μ_{th} (eV)	
S_2	-3.8 $(0/+)$	-1.4 $(-/0)$
S_3	-4.1 $(0/+)$	-1.8 $(-/0)$
V_2	-3.8 $(0/+)$	-1.5 $(-/0)$
V_3	-1.8 $(0/+)$	0.4 $(-/0)$
$S_{2\mathrm{O}}$	-2.6 $(0/+)$	-0.2 $(-/0)$
$S_{2\mathrm{H}}$	-4.0 $(0/+)$	
$S_{3\mathrm{H}}$	-4.0 $(0/+)$	
$V_{2\mathrm{H}}$	-2.5 $(0/++)$	
$V_{3\mathrm{H}}$	-4.3 $(0/+)$	
$S_{2\mathrm{OH}}$	-2.7 $(0/+)$	

thermodynamic levels [17], are summarized in Table I. The thermodynamic levels in Fig. 2 are aligned with respect to band edges, by matching the theoretical and experimental thermodynamic levels related to the interstitial H in $\mathrm{SiO_2}$, located at 0.2 eV above the Si midgap (the energy reference hereafter), and by using the valence-band offset of 4.3 eV between $\mathrm{SiO_2}$ and Si (refer to Ref. [17] for details).

The thermodynamic level defined above is not a single-electron level obtained by the Kohn-Sham equation. The Kohn-Sham (KS) level near μ_{th}, however, provides the chemical understanding of changes in charge states since the charge-state changes are processes of carrier capture or emission through some electron state in the gap. We will show analyses of the wave functions of such KS levels for the neutral defects below.

We begin with the V_2 structure since an O vacancy is proposed to be responsible for SILC in $\mathrm{SiO_2}$. The KS levels are originated from the LP-like (LPL) and DB-like (DBL) states of N and from the Si-Si dimer bond [29]. The LPL state of N with the minority spin, located at -2.4 eV, can capture an electron under electron injection since it is empty in the neutral state [Fig. 3(a)]. The filled DBL state of N with the minority spin, located at -3.1 eV [Fig. 3(b)], can release an electron and then play the role of a hole trap. The Si-Si dimer states of both spins are below the above two states. It is notable that the neutral charge state has the spin $S = 1/2$ and that the positive charge state has $S = 1$, due to the spin polarization of the LPL and DBL states (the Hund rule). For the doubly positive charge state, the V_2 structure transforms to the V_3 structure with the breaking of the Si-Si bond. This bistability is also observed for an O vacancy in $\mathrm{SiO_2}$ [15,16]. The charging characters of the S_2 structure are the same as those of the V_2 structure (except for $Q = 2$) because both structures contain the twofold N atom that provides the charge traps.

The V_3 structure has different features in the KS levels from the V_2 structure. Instead of the disappearance of the DB states of the N atom, the DB states of the right Si atom emerge at -1.7 eV for the majority spin and at 0.7 eV for the minority spin [Fig. 3(c)]. The LP states of the N atom still remain in the $\mathrm{SiO_2}$ energy gap [Fig. 3(d)]. Thus the DB of the right Si atom can capture both an electron and a hole, depending on the position of the Fermi energy. The positively charged structure, in this case, is spin unpolarized, unlike the V_2 and S_2 structures.

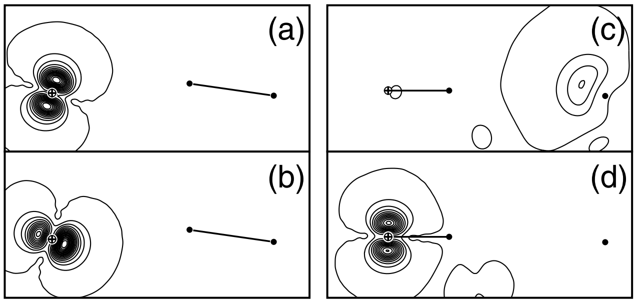

FIG. 3. Contour plots of the squared wave functions for (a),(b) the lowest unoccupied and highest occupied KS levels with the minority spins of V_2 (-2.4 and -3.1 eV, respectively) and (c),(d) the lowest unoccupied and second-highest occupied KS levels with the minority spins of V_3 (0.7 and -3.6 eV, respectively). The contour plane passes through the N atom (crossed circles) and bisects the (rough) equilateral triangle defined by the N atom and the two Si atoms bonded to N. The filled circles denote the positions of Si atoms near the O vacancy (see Fig. 1). All the atoms within ±0.2 Å from the contour plane are displayed. The contour spacing is $0.01e/(\mathrm{a.u.})^3$.

In the S_3 structure, we verify that the LPL of O and the LP of N become the electron and hole traps, respectively. In the $S_{2\mathrm{O}}$ structure, the antibonding states between the LPs of the N atom and its neighboring O atom, located at -0.9 and -2.1 eV, become charge traps under electron or hole injection.

The N-incorporated structures hereby induce the gap states which play the roles of charge traps. The occupancy of the charge trap states is sensitive to the position of the Fermi energy that changes according to the external bias voltage across the oxide films. At zero bias, corresponding roughly to $\mu = 0$, the negative charge states are the most stable, except for V_3. Within relatively small magnitudes of bias ($\sim 0.2 - 1.8$ V, Table I), the atomic structures change their charge states from the negative to the neutral. Larger biases then induce the charged states from the neutral to the positive. This shows that the N incorporation in Si oxides itself is inadequate to erase carrier traps and then improve electrical reliabilities of the gate dielectrics.

The N-incorporated structures become much more stabilized by capturing a H atom at the sites depicted in Fig. 1. The H-terminated structures have lower energies by $\sim 2.8 - 4.1$ eV than the corresponding H-free structures [24] plus $\mathrm{H^+}$ in $\mathrm{SiO_2}$ [24,30]. As shown in Fig. 2 and Table I, the H termination gives rise to remarkable changes in electronic structures and, consequently, in structural stabilities. All the DB states disappear from the energy gap because of the formation of strong bonds with H. As a result, we have only the gap states from the LP of N in $S_{2\mathrm{H}}$, $S_{3\mathrm{H}}$, and $V_{3\mathrm{H}}$ and from the Si-Si dimer bond and the LP of N in $V_{2\mathrm{H}}$. These remaining gap states are in the

SiO_2 energy gap. However, they are practically inactive for a wide range of applied voltage due to their sufficiently deep positions in the energy gap [see Figs. 2(b) and 2(d) and Table I]. Further, since all the gap states are already occupied, electrons are unable to be trapped for the whole range of the Fermi energy. Therefore, in the H-terminated structures, $S_{2\mathrm{H}}$, $S_{3\mathrm{H}}$, and $V_{3\mathrm{H}}$, the carrier traps are effectively removed from the practical range of the Fermi-level position. This is in agreement with a recent voltage shift measurement for the gate dielectrics grown on the N-implanted Si substrate [3].

The $N{\equiv}Si_3$ unit, observed as the most dominant species in Si oxynitride, is found to be effective in reducing the charge traps, only if it is *terminated* by H ($V_{3\mathrm{H}}$ and $S_{3\mathrm{H}}$). The $H{-}N{=}Si_2$ unit, although regarded experimentally as a minor species, is also effective. Difference of the N 1*s* core levels between $H{-}N{=}Si_2$ and $N{\equiv}Si_3$ is calculated as about 0.6 eV [13,31], which falls into the experimental core-level peak distributions. Thus, the $H{-}N{=}Si_2$ unit cannot be manifestly excluded at the present stage [13]. The existence of N-O bonds, on the contrary, is not desirable for suppression of charge trapping: We have found that the antibonding states of LPs of the N and O atoms in the $S_{2\mathrm{O}}$ structure become hole traps that are still active for a bias as small as 2.7 V, even after H termination. Of course, it is impossible that the present models cover all the possible bond configurations around N, especially near the SiO_2/Si interface. But we argue that the calculated results are directly extended to other structures and that the charging characters can be predicted based on the generic features of the present model structures.

H termination (without N incorporation), although generally effective in removing the gap states of DBs from the energy gap, does not automatically guarantee suppression of charge trapping. A recent DFT calculation showed that the H-complexed O vacancy, where two Si atoms that were bonded to the removed O atom (O vacancy) are terminated by two H atoms, is susceptible to hole injection, through formation of a H_2 molecule [18]. In addition, another calculation proposed that the H bridge at an O vacancy, where a H atom enters the O vacancy site and is bonded to two Si atoms, is a source of charge trapping [17]. Based on the present DFT calculations as well as those explained above, we thus argue that the improvement in electrical reliabilities of Si oxynitrides originates from the *coexistence* of N and H, neither from the presence of N alone nor from the presence of H alone.

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