Nitrogen-induced interface defects in Si oxynitride

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Based on first-principles density-functional calculations, we propose N-associated defects at Si/SiO_2 interface, which behave as dominant interface states in Si oxynitrides instead of conventional P_b centers in pure SiO_2. These defects involve an N interstitial, and their energy levels lie in the broad range, from the midgap to the conduction-band edge of Si, depending on local oxidation status near N, while electrical states from P_b-type centers are removed by substitutional N atoms. Our results provide a mechanism for degradations related to the interface defects in Si oxynitrides which are used in state-of-the-art metal-oxide-semiconductor devices.

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Defects at Si/SiO_2 interface have been intensively studied for several decades because they act as an interface charge trap which degrades performances and reliabilities of metal-oxide-semiconductor (MOS) transistors. It is well identified by experiments and theories[1–5] that dominant interface defects, the so-called P_b centers, are isolated dangling bonds from Si substrate near the interface.

Unfortunately, a further study on the interface traps becomes required, as Si oxynitride (or lightly nitrided oxide) has replaced pure SiO_2 in state-of-the-art MOS transistors that are used in commercial semiconductor devices. The nitridation of SiO_2 is essential for suppressing boron penetration from p^+-polysilicon electrodes.[6] In addition, it also improves electrical properties such as charge trapping,[7] and theoretical models for this effect have already been given.[8,9] On the other hand, the N incorporation at the interface is known to increase densities of interface traps,[10] causing performance degradations and reliability problems.[11–14]

Recent experiments clearly show that new interface defects are created and act as dominant species in Si oxynitrides instead of P_b center. Stathis *et al.* showed that the interface states are located near the conduction-band edge of Si with a broad energy distribution, through low-voltage stress-induced leakage current (LV-SILC) measurements, while pure oxide shows negligible interface state generation at the conduction-band edge.[15,16] On the other hand, the defect density at midgap is much larger in SiO_2, as compared to that in oxynitride.[15,16] Campbell *et al.* also observed a new defect center in oxynitride which is fundamentally different from P_{b0}/P_{b1} defects,[17] through electron spin resonance measurements. Understanding the N-related interface defects on an atomistic level is very important to modern MOS technology, but these defects are not clearly identified yet.

In this paper, we present an atomic model for N-induced defects at the interface between Si and Si oxynitride based on first-principles density-functional calculations. We find that N interstitials at the interface create defect levels in the Si band gap, which move upward from the midgap to the conduction-band edge, as the interactions with oxygen atoms in SiO_2 matrix are enhanced. On the other hand, the deep defect level caused by a P_b-like center, i.e., a threefold-coordinated Si, is removed by substitution of an N atom. Our model for N-associated interface defects explains the enhanced interface state generation near the conduction-band edge and the reduction of midgap defect density in Si oxynitrides.

First-principles pseudopotential calculations are performed using density-functional theory (DFT) within the generalized gradient approximation.[18] We use ultrasoft pseudopotentials for O, N, and H (Ref. 19) and a norm-conserving pseudopotential for Si.[20] A converged plane wave basis set is generated with energy cutoffs of 30 Ry for wave functions and 180 Ry for charge densities, respectively. To describe Si/SiO_2 interface, we construct the interface with Si crystal and tridymite SiO_2 in a supercell containing 128 atoms, similar to the previous theoretical studies.[21,22] This supercell geometry is a periodic slab structure with seven Si layers for bulk Si and two Si and four O layers for SiO_2, and the Si dangling bonds at both surfaces are passivated by H atoms. The Si band gap of this interface is found to be 1.05 eV, similar to previous calculations.[21] This value is larger than for usual DFT band gap of bulk Si because of the quantum confinement effect in the slab geometry.[21]

First, we study electronic and atomic structures of an N interstitial (N_i) and its complexes with oxygen ions at the interface. When an N interstitial is incorporated deep into the Si layers in our interface model, it is found that a (100)-split-interstitial geometry is the most stable, similar to previous calculations on N in Si.[23,24] A symmetric split-interstitial structure at the interface has difficulty maintaining its stability because of lattice strain near the interface. The optimized structure of the N_i at the interface is illustrated in Fig. 1(a). This defect also includes a trivalent N and Si atom, similar to the (100) split interstitial, and the threefold Si atom (Si_I) protrudes into the SiO_2 side. Si_I is undercoordinated and, thus, a chemically active atom in the defect, while the valence shell of N is completely filled. Due to the asymmetric structure, the Si_I-Si_{III} distance (3.15 Å) is longer by 0.52 Å than the Si_I-Si_{II} distance (2.63 Å). A charge density analysis indicates that no bonding occurs between Si_I and Si_{II}, although the distance between them is only longer by 0.3 Å than the Si-Si bond length in crystalline Si. The Si-N bond lengths are found to be 1.73–1.85 Å, and nearest-neighbor Si-Si bonds from N are elongated by 0.08 Å to compensate for lattice strain caused by these short Si-N bonds. If posi-

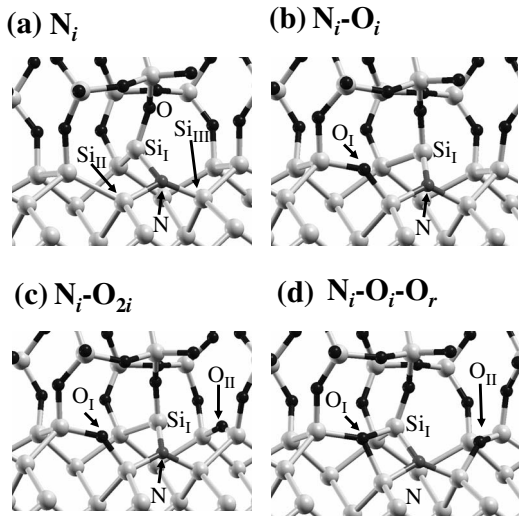

FIG. 1. Atomic structures of the (a) N_i, (b) N_i-O_i, (c) N_i-O_{2i}, and (d) N_i-O_i-O_r defects at the interface.

tions of the Si_I and N atom are changed in Fig. 1(a), that geometry would be unrealistic due to the unstable N-O bond, which are not supported by theoretical studies.[25,26] In fact, we investigated a number of geometries of N_i at other Si sites at the interface for various bonding directions and did not find any significant difference from the structure in Fig. 1(a).

For partially oxidized interface, it is energetically favorable that N_i forms a complex with O ions. We model partial oxidation of the interface by using O interstitials (O_i) incorporated at the Si-Si bonds because our supercell does not include O atoms at the interface, i.e., the top layer of Si. For N_i-O_i complex, the O interstitial prefers the nearest Si-Si bond sites from the N_i, as shown in Fig. 1(b); the total energy is lowered by 0.62 eV than for an isolated O_i at the same Si layer and an isolated N_i because of a coordinate covalent bonding of Si_I with the O_i. Thus, nearest-neighbor Si-Si bonds from N are expected to behave as attracting centers for O ions in partially oxidized interfaces. The Si_I atom is shifted away by 0.37 Å from its initial position to reduce repulsive Coulomb interaction with the lone-pair orbital of O_I. When the second O ion (O_{II}) is incorporated at another nearest-neighbor bond from N, Si_I and O_I atoms become fourfold and threefold coordinated, respectively, by forming the Si_I-O_I bond [see Fig. 1(d)]. We refer to this structure as N_i-O_i-O_r complex, where O_r means a threefold-coordinated O atom. The complex is more stable by 1.04 eV than an isolated N_i and two isolated O_I. This structure is similar to that of the O_i-O_{2r} complex, which is shallow thermal donor in Si,[27,28] if N is replaced by an O atom. The N_i-O_{2i} structure, in which Si_I-O_I is broken, is found to be unstable in the same O_i positions because of lattice strain near the interface, although the similar defect, N_i-O_{2i} with C_{2v} symmetry, is suggested to be stable in bulk Si.[23,24] On the other hand, the N_i-O_{2i} complex becomes stable, when O_{II} moves to the second-nearest-neighbor Si-Si bond, as shown in Fig. 1(c). This defect is less stable by 0.16 eV than for N_i-O_i-O_r. We find that an isolated O_{II} at the first Si layer is more stable by 0.18 eV than an isolated O_I at the second Si layer. Compared to N_i-O_i plus an isolated O_{II}, the binding energy of N_i-O_{2i} is found to be 0.08 eV. It increases to 0.26 eV, as referenced to an isolated O_I and N_i-O_i. The Si_I-O_{II} distance, 3.47 Å, is not much different from other Si-O distances lying in the range of 3.32–3.36 Å except for the Si_I-O_I distance of N_i-O_i-O_r (see Table I). The interaction between Si_I and O_{II} is also found in the defect level, shown in Fig. 2(a), where the lone-pair orbital of O_{II} is hybridized. Because of exothermic binding energies, N interstitials might form complexes with oxygen ions at the interface. The main features found here are expected to be unchanged even for amorphous SiO_2 because the geometries of N_i-related defects are mainly determined at the silicon side of the interface, as exhibited in Figs. 1(a)–1(d).

TABLE I. Single-particle defect levels (E_{KS}), defect transition levels ($E_{-/0}$) between neutral and negatively charged states, and Si-O distances for N_i-related defects. E_c indicates the conduction-band minimum of Si.

Defect	E_{KS} (eV)	$E_{-/0}$ (eV)	Distance (Å)	
			Si_I-O_I	Si_I-O_{II}
N_i	$E_c-0.4$	$E_c-0.31$		
N_i-O_i	$E_c-0.29$	$E_c-0.20$	3.36	
N_i-O_i-O_r	E_c	E_c	1.85	3.33
N_i-O_{2i}	$E_c-0.19$	$E_c-0.12$	3.32	3.47

Here, we find that energy levels of N_i-associated interface defects are shifted upward in Si band gap, as interactions with O ions are enhanced. The shifts of defect levels do not result from direct interactions between N_i and O_i, but from the interactions of threefold Si atoms created by N_i with O_i. To deal with charge capture process via nonequilibrium tunneling process, we analyze the single-particle defect levels of neutrally charged defects. The calculated defect levels for the N_i-related defects are listed in Table I, as referenced to the bottom of the conduction band (E_c). For N_i, a deep defect level is found at $E_c-0.4$ eV. The level does not arise from the N atom itself but from the dangling bond of the threefold Si atom, similar to the N_i-O_{2i} characterized in Fig. 2(a). For N_i-O_i, the defect level is elevated by 0.11 eV because of the Coulombic repulsion between the lone-pair orbital of O_I and the dangling bond of Si_I. Contrary to our results, it is re-

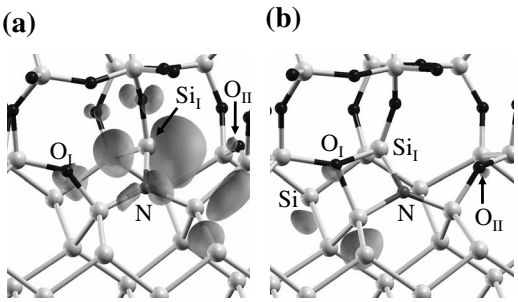

FIG. 2. Charge densities are plotted for the defect levels of the (a) N_i-O_{2i} and (b) N_i-O_i-O_r defects for an isosurface of 0.002 a.u.

ported that the defect state becomes deeper for bulk Si after the formation of N_i-O_i complex;[24] this is attributed to the fact that the dangling bond orbital of N_i-O_i becomes more localized after the symmetry of the N_i is broken. For the N_i-O_i-O_r defect, it is found that a shallow-level interface state near E_c is created. The physical origin of the shallow interface state can be explained as follows; as shown in Fig. 1(d), this defect contains no undercoordinated Si atom and thereby does not have the defect level associated with the Si dangling bond. Instead, one excess electron is left after filling the valence shell of overcoordinated O_I, and this electron may be transferred to an antibonding orbital of Si_I and O_I. However, since this antibonding orbital [Fig. 2(b)] lies above the conduction band, the electron may occupy the conduction band and thus the creation of the shallow level is expected by the effective mass theory. The key component of the shallow-level defect is the threefold-coordinated oxygen atom. If O_I in N_i-O_i-O_r is replaced by a N atom, the defect has no undercoordinated or overcoordinated atoms; the Si, N, and O atoms are fourfold, threefold, and twofold coordinated, respectively. Thus, this defect might be an electrically inactive complex with no defect levels in the Si band gap. Although the chemical structure of N_i-O_i-O_r is almost identical to that of this inactive defect, the threefold O atom (O_r) has one more electron than the N atom. Since N_i-O_i-O_r has no defect levels in the band gap, it is expected that the shallow level just below the conduction band is created, similar to the phosphorus defect in Si. Other interface defects involving a stable threefold O atom might also have shallow defect levels near the conduction band. For the N_i-O_{2i} complex, the defect level moves down to 0.19 eV below the conduction-band minimum, as the bond of the Si_I and the O_{II} atoms is broken. However, it is still affected by O_{II}, as discussed earlier, and thereby higher by 0.1 eV than for N_i-O_i. We also analyze thermodynamic defect transition levels, which are obtained from the energy difference of two relaxed geometries with different charges. The transition levels between neutral and negative charge states are calculated because these levels describe the electron tunneling from interface traps below the *n*-well Fermi level into the p^+-polysilicon electrode, which leads to the LV-SILC in *p*-type metal-oxide-semiconductor field-effect transistor.[15] As listed in Table I, the calculated transition levels are pushed upward from $E_c-0.31$ eV to E_c, as the interaction with O ion is enhanced, similar to the single-particle levels. Thus, our results show that energy levels of N_i-related defects possibly lie in the broad energy range from the midgap to conduction-band edge, depending on the degree of interactions with O ions. For amorphous SiO_2, more broad level distributions are expected because of more various local configurations of oxygen atoms.

On the other hand, we find that a substitutional N atom possibly removes electrical activity of an interfacial Si dangling bond, the so-called P_b center, as reported in previous theoretical calculations,[29] although the N_i-related species act as an interface trap. In our previous calculations, we suggest that most of the substitutional N atoms (N_{Si}) exist as an N pair at interface, while single N is unstable due to the creation of a dangling bond.[8] However, single substitutional N is stabilized, when it replaces a threefold-coordinated Si with

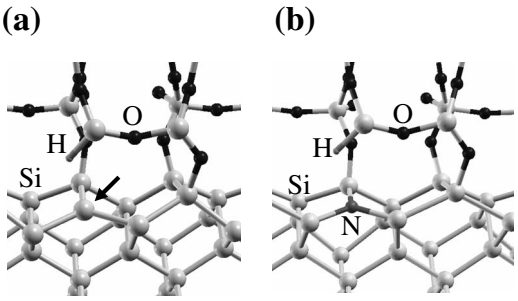

FIG. 3. Atomic models of the (a) P_b center and (b) N_{Si} at the interface. The arrow in the figure indicates a threefold-coordinated Si.

an unpaired dangling bond. To validate this argument, we first construct a model geometry for P_b center as in Fig. 3(a). This model is similar to the dimer model for the P_{b1} defect in the previous calculations,[5] but our conclusions are not affected even if other interface models are used. We find that undercoordinated Si is possibly replaced by a threefold N atom without any remaining dangling bond orbital, as shown in the N_{Si} defect [see Fig. 3(b)]. This defect is an electrically inactive center with no defect level in the band gap, while a deep level is found at $E_c-0.4$ eV for our P_b center model. We investigate the stability of N_{Si} defect via the reaction, P_b center + N_i (at the interface) $\rightarrow N_{Si}$ (at the interface) + Si (of perfect crystal), and find that this reaction is exothermic by 1.93 eV. Thus, the annihilation of the P_b center by substitution of N is energetically favorable in Si oxynitride.

The experimentally reported interface states and suppressed P_b centers in Si oxynitrides are explained by our proposed models for N-interstitial-related and substitutional N defects, respectively. In LV-SILC and gated diode measurements, the interface states in oxynitrides are found to be distributed over a broad energy range in the upper portion of the Si band gap.[15] We showed that the defect levels for the N_i-related species are possibly located at various positions between the midgap and the conduction-band edge, depending on interactions with neighboring O atoms, in good agreement with the experiments. Among the defects distributed over the broad range, it is expected that the concentrations of conduction-band edge defects such as N_i-O_i-O_r are higher than for midgap defects due to the following reasons. The isolated N interstitial produces a deep interface state, but it is only stabilized at the oxygen-free interface like Fig. 1(a), where the top layer of Si bears no oxygen atom. For a partially oxidized interface, which is usually expected in normal oxidation process, N_i might attract O atoms because of the exothermic binding energies, and thus the defect levels are pushed upward by the interactions with O atoms. Especially, defects involving trivalent O atoms might greatly enhance LV-SILC, since they possess defect levels close to the conduction band. The suppression of midgap states[16] is explained by the removal of P_b-center-like defect by substitutional N atoms. However, electrical improvement of the interface is not guaranteed by the removal of P_b centers, since the N_i-associated species possibly degrade interface properties. Our N-defect models only involve $N\equiv Si_3$ species, i.e., one N bonded to three Si atoms, in good agreement

with x-ray photoelectron spectroscopy measurements for interfacial N atoms, while the chemical bond of N away from the interface is possibly to be either N bonded to two Si and one O atom (O-N═Si_2) or N bonded to two Si atoms (N═Si_2).[25,26,30–33] Thus, our calculations successfully explain the recent experiments for the N-related species in ultrathin Si oxynitrides which have not been fully understood.

In conclusion, we investigate the N-induced defects at the Si/SiO_2 interface through *ab initio* pseudopotential calculations. We find that the N interstitials at the interface create various defect levels in the Si band gap, which range from the midgap to the conduction band of Si. The level positions are dependent on the configuration of oxygen atoms around the N interstitial. On the other hand, the midgap level caused by P_b center is possibly removed by substitution of an N atom for a threefold-coordinated Si atom in the defect. Our calculations explain why the interface state generation is enhanced in Si oxynitride, especially near the conduction-band edge of Si, although the density of P_b center is reduced.

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