Electrically inactive nitrogen complex in Si oxynitride

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Based on first-principles theoretical calculations, we find a very stable nitrogen complex in oxynitrides, which consists of two N atoms at O sites and one O vacancy. This N complex is electrically inactive without bonding with hydrogen, removing the electrical activity of O vacancies, and the stability of this complex is greatly enhanced as going from pure oxide to oxynitride films. We suggest that charge traps involving a single N atom, such as a bridging N center, can be deactivated by reactions with O or NO interstitials, and resulting N interstitials are easily depleted into the interface, in good agreement with experiments.

The incorporation of N into a gate oxide of metal-oxide-semiconductor (MOS) devices has attracted much attention because of the suppression of dopant diffusion, leakage current, charge trapping, and hot-carrier-induced degradation.[1–5] Experiments showed that the performance of MOS devices depends on both the concentration and distribution of N incorporated in oxynitride (or lightly nitrided oxide) films.[6] However, the reason for the electrical improvement of MOS devices by N incorporation is not clearly understood, while it desires a complete understanding of the structural and electronic properties of oxynitrides on an atomic level.

There have been much debates on the bond configuration of incorporated N. From x-ray photoelectron spectroscopy measurements for oxynitrides,[7,8] a $N{\equiv}Si_3$ configuration was suggested at or very close to the interface, i.e., one N bonded to three Si atoms, while the chemical bond of N away from the interface is either a N bonded to two Si and one O atom ($O{-}N{=}Si_2$) or a N bonded to two Si atoms ($N{=}Si_2$).[6,9–11] Previous theoretical calculations indicated that N incorporation in SiO_2 generates dangling bonds or lone pairs of the Si, O, and N atoms, and hydrogenation deactivates these charge traps.[12] However, H-related bonds such as Si-H and N-H have not been observed in oxynitride films grown in N_2O ambient,[13,14] which exhibit smaller electron and hole trap densities, as compared to pure SiO_2 film. In NH_3-nitrided films, on the other hand, a much higher charge trap density was found, with a large number of Si-H and N-H bonds formed by the introduction of high H concentrations.[13,14] Since H densities are usually lower in N_2O-oxynitrided films, it is unlikely that H plays an important role in reducing charge traps in these samples.

In this paper, we present an atomic model for N incorporated in SiO_2, based on first-principles pseudopotential calculations. We find a very stable N-related complex near the interface, which consists of one O vacancy and two N atoms in the $N{\equiv}Si_3$ configuration. This complex is an electrically inactive center with no dangling bond even in the absence of H, and becomes very stable as going to Si-rich layers, where the concentration of N is increased. Due to the inactive N-related complex, the electrical activity of O vacancies is severely suppressed, explaining experimental findings that the intensity of partially oxidized Si atoms and the density of E′ centers near the interface are significantly reduced. We suggest that O or NO interstitials easily deactivate charge

traps involving a single N atom, and depleted N atoms moves to the interface to form the inactive N complex.

We calculate the total energies of N-related defects in α-quartz SiO_2 using a first-principles pseudopotential method within the generalized gradient approximation.[15] To deal with the localized nature of the O- and N-$2p$ orbitals, we use a real-space multigrid method,[16] which has been very efficient in applications to localized systems such as SiO_2 and ZnO.[17,18] The Laplacians in Poisson and Kohn-Sham equations are expressed up to the 12th order, based on a higher-order finite difference method.[19] We employ the same set of grids as that used for a 72-atom supercell in previous calculations for SiO_2.[17] With use of the conjugate-gradient technique, we relax ionic coordinates until the atomic configuration is optimized. The formation energy of a defect α is defined as,[20] $E_f(\alpha){=}E_{(tot)}(\alpha){-}\Sigma_\beta n_\beta \mu_\beta$, where $E_{(tot)}(\alpha)$ is the total energy of the supercell containing the defect α, n_β is the number of β atoms ($\beta{=}Si$, O, and N) in the supercell, and μ_β is the chemical potential of a β atom. The chemical potentials of bulk Si and O_2 are chosen as the maximum values for μ_{Si} and μ_O, respectively, and satisfy the relation, $\mu_{Si}{+}2\mu_O{=}\mu_{SiO_2}$, where μ_{SiO_2} is the total energy per molecule in SiO_2. To describe the stoichiometry of SiO_2, we use the stoichiometric parameter λ defined as μ_{Si} $={\mu_{Si}}(bulk){-}\lambda\Delta H$, where $\mu_{Si}(bulk)$ is the chemical potential of bulk Si and ΔH is the calculated heat of formation of α quartz, 9.53 eV. Since NO molecules are considered to be responsible for oxynitridization in both N_2O- and NO-grown oxynitride films,[21] we obtain the N chemical potential from that of a NO molecule, $\mu_N{=}\mu_{NO}{-}\mu_O$.

First, we study the energetics of the $N{=}Si_2$ and $N{\equiv}Si_3$ configurations, which involve a single N in bonding. In the $N{=}Si_2$ class, the most preferential species are drawn in Figs. 1(a,b), referred to as $N(2)_O$ and $N(2)_O$-V_O, which represent the twofold N atoms at the O lattice in the perfect α quartz and α quartz with an O vacancy (V_O), respectively. Similarly, the threefold N atoms in the $N{\equiv}Si_3$ configuration are referred to as $N(3)_O$ and $N(3)_O$-V_O in Figs. 1(c,d). In general, the Si-N bond lengths of the twofold N atoms are found to be 1.66–1.67 Å, while they increase to 1.73–1.80 Å for the threefold N atoms, similar to previous calculations.[12] In the $N(3)_O$ and $N(3)_O$-V_O defects with a broken bond, a new bond between the N and Si_I atoms is formed, and a six-
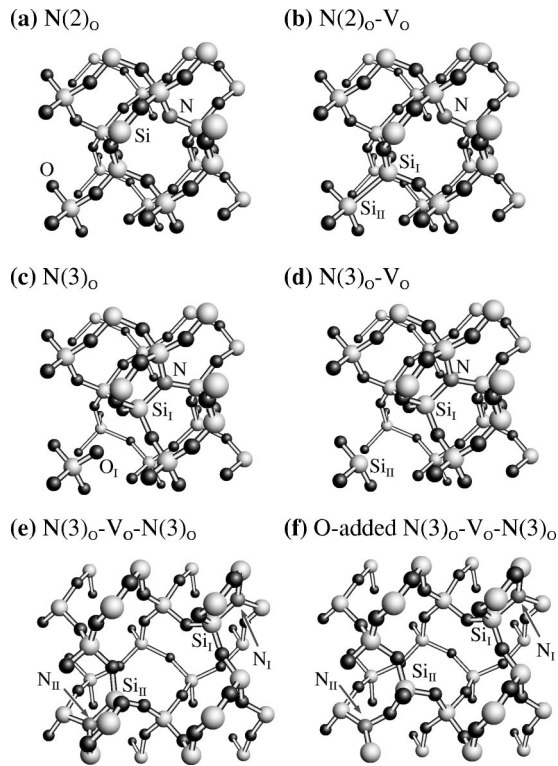
FIG. 1. Atomic structures of the (a) $N(2)_O$, (b) $N(2)_O$-V_O, (c) $N(3)_O$, (d) $N(3)_O$-V_O, (e) $N(3)_O$-V_O-$N(3)_O$, and (f) O-added $N(3)_O$-V_O-$N(3)_O$ defects in the α-quartz structure.

member ring containing the N atom split into three- and four-member rings. Since a Si-O bond is stronger than a Si-N bond, the formation energy of $N(2)_O$ is lower by 1.85 eV than for $N(3)_O$, as shown in Fig. 2. When the Si_I-N bond is formed as going from $N(2)_O$-V_O to $N(3)_O$-V_O, it gains a much higher energy than the energy cost to break the Si_I-Si_{II} bond, thus, the $N(3)_O$-V_O defect has the formation energy lower by 1.74 eV. Among the N=Si_2 and N≡Si_3 defects up to now, $N(2)_O$ has the lowest formation energy over the whole range of λ, except for the extreme Si-rich region ($\lambda \approx 0$), where $N(3)_O$-V_O is stabilized by reaction with V_O.
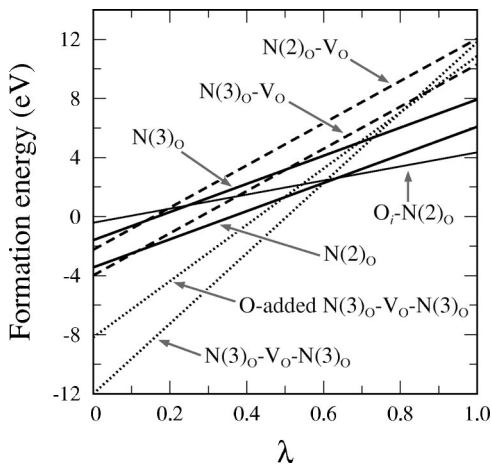

FIG. 2. The formation energies of various N-related defects as a function of the stoichiometric parameter λ.
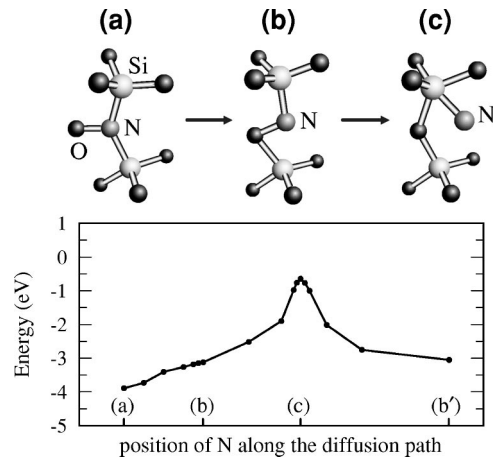

FIG. 3. Atomic structures of the (a) O_i-$N(2)_O$, (b) N interstitial in the peroxy linkage structure, and (c) transition state with a N bonded to a Si atom. The lower panel shows the variation of energy along the diffusion path of N, where (b') denotes other peroxy linkage structure with the N positioned at a neighboring Si-O-Si bridge site.

However, all these defects contain active dangling bonds, becoming charge trap centers, while it was suggested that *H* incorporation prevents the charge trap generation.[12]

Here, we find a *H*-free defect complex that solely consists of N and V_O, without any dangling bond. This complex, referred to as $N(3)_O$-V_O-$N(3)_O$ in Fig. 1(e), has two three-fold N atoms (N_I and N_{II}) on both the sides of V_O. Because of the two N≡Si_3 species, this complex is an electrically inactive center, with no defect level in the band gap, very similar to donor-vacancy complexes proposed for inactive donors in Si.[22] If N_I and N_{II} change into two $N(2)_O$ species, the Si_I-Si_{II} bond is recovered. However, since lone-pair states remain at the twofold N atoms, the total energy increases by 6.20 eV, indicating that $N(3)_O$-V_O-$N(3)_O$ is a very stable complex. When an O atom is added to the N_{II}-Si_{II} bond, the N_{II} atom forms a bond configuration of O—N=Si_2 [see Fig. 1(f)]. This O-added complex is less stable than $N(3)_O$-V_O-$N(3)_O$ for a wide range of λ, while it is stabilized against $N(2)_O$ for $0 < \lambda < 0.5$, as shown in Fig. 2. We also consider adding an O atom to the $N(2)_O$ defect, which is referred to as O_i-$N(2)_O$ in Fig. 3(a), and find that this N configuration is the most stable defect for λ above 0.64, i.e., under the O-rich condition.

For N concentrations larger than 10^{14} cm^{-3}, which can be achieved for $\lambda < 0.6$ at a growth temperature of 1000 °C [see Fig. 2], the $N(3)_O$-V_O-$N(3)_O$ complex is found be the most stable N configuration. The stability of this complex is greatly enhanced against $N(2)_O$ as going to the Si-rich limit. This result indicates that N is likely to be incorporated in the Si-rich region such as suboxide layers near the interface, in good agreement with experiments.[23] Using a Si/tridymite-SiO_2 interface model, we find that an inactive $N(3)_{Si}$-$N(3)_{Si}$ complex, where two adjacent Si atoms are occupied by two N atoms, can be formed in the Si bulk region close to the interface, similar to an inactive pair of phosphorous.[24] The binding energy of this complex is calculated to be 1.98 eV, as compared to two isolated substitutional $N(3)_{Si}$ atoms. If the

$N(3)_{Si}$-$N(3)_{Si}$ complex is buried in oxynitride as the interface grows into the Si substrate, it is expected to gradually transform into the $N(3)_O$-V_O-$N(3)_O$ complex. The existence of N≡Si_3 units in the $N(3)_O$-V_O-$N(3)_O$ complex agrees well with x-ray photoelectron spectroscopy measurements[11] and theoretical calculations[9,10] of core-level shifts. When the $N(3)_O$-V_O-$N(3)_O$ complex is formed via the reaction, $3V_O + 2N_i$ [or $2N(2)_O + V_O$]→$N(3)_O$-V_O-$N(3)_O$, which is found to be exthothermic by 15.95 eV, O vacancies in incompletely oxidized Si are annihilated by nitridization, consistent with the prediction by the Mott rule.[25] The annihilation of O vacancies also agrees with other experiments, which reported that N incorporation significantly reduces the density of partially oxidized Si atoms in the suboxide layer near the interface,[7] and removes the E' centers,[26] which are regarded as positively charged O vacancies,[27] especially near the interface. In the amorphous environment, it is expected that the pair of threefold N atoms may not have the same structure as that obtained in crystalline quartz. Because of the continous random network, the two threefold N atoms in the pair may be separated more than that in crystalline quartz. Then, it may appear that the threefold N atoms look isolated defects, which is not inconsistent with the single threefold N defect model.[9,10] Our results suggest that the defect center with two threefold N atoms is the most dominant inactive N defect in amorphous Si oxynitride. However, since the structure of amorphous film is different from that of crystalline quartz, other possibilities such as the creation of the inactive single threefold N defect can not be ruled out. Thus, more decisive experiments are required to clarify the atomic structure of the dominant inactive N defect.

Oxide films grown in N_2O by rapid thermal oxidation (RTO) have a preferential pileup of N at the Si-SiO_2 interface, while furnace-grown oxides in N_2O exhibit a fairly uniform distribution of N throughout the oxide.[6,8,28] Among the gas-phase products decomposed from N_2O by RTO, such as N_2, O_2, NO, and O, Carr and co-workers suggested that a reaction involving atomic O depletes previously incorporated N from the oxide.[8] They also showed that incorporated N in the oxide is removed by annealing in O_3, which produces atomic O, while the N distribution is not significantly affected by O_2. Other view based on a reaction involving NO for the N removal was given,[29] while other experiments reported that the supply of NO does not remove N.[28]

To see the depletion of N by atomic O, we examine the reaction of N-related defects acting as a charge trap with interstitial O, and the subsequent diffusion of N as an interstitial. When $N(2)_O$ forms the O_i-$N(2)_O$ complex [see Fig. 3(a)] with an interstitial O, the energy is lowered by 3.89 eV. Figure 3 shows the variation of energy along the diffusion path of N in the O_i-$N(2)_O$ complex, relative to isolated O_i and $N(2)_O$. For each position of the path between two (meta)stable configurations, the geometry optimization is performed by constrained conjugate-gradient relaxation method.[30] As the O_i-$N(2)_O$ defect turns into a peroxy linkage structure with the N atom incorporated in the Si-O-Si bond [see Fig. 3(b)], the energy increases gradually by 0.77 eV, while the energy of a threefold configuration, where N is directly bonded to the O atom, is much higher by 2.97 eV. In

the peroxy linkage structure, the N interstitial migrates to a neighboring Si-O-Si bridge site and forms a new peroxy linkage, with an energy barrier of 2.47 eV. At the saddle point of this diffusion process, the N atom is only bonded to the neighboring Si atom [see Fig. 3(c)], very similar to the concerted exchange of O interstitial,[31] and eventually diffuses into the interface along the SiO_2 network. Since the kick-out diffusion of N by O_i occur with energies much lower than that of isolated $N(2)_O$ and O_i, it is very likely for the $N(2)_O$ defect to be depleted in the oxide by reaction with atomic O. Similarly, for other N-related defects involving a single N atom, we find the formation of O_i-$N(2)_O$ via exothermic reactions with interstitial O, which results in a similar O-assisted diffusion of N; the reactions of $N(3)_O+O_i$, $N(3)_O$-V_O+2O_i, and $N(2)_O$-V_O+2O_i are exthothermic by 5.74, 10.26, and 12.00 eV, respectively. Our results indicate that the O-assisted diffusion of N is highly likely to occur in the RTO process using N_2O, where atomic O is supplied from the decomposition of N_2O.[8] When the N atom diffuses into the interface, where O vacancies are piled up, O vacancies will be annihilated by the reaction, O_i-$N(2)_O+3V_O$ →$N(3)_O$-V_O-$N(3)_O$, which is exothermic by 14.41 eV. Since the oxynitridization or annealing process induces the formation of the inactive $N(3)_O$-V_O-$N(3)_O$ complex, the charge traps associated with O vacancies near the interface are deactivated.

We also find that the $N(2)_O$ defect is easily removed by reaction with an interstitial NO molecule, as suggested by Saks and co-workers.[29] When $N(2)_O$ forms a complex with NO, the binding energy is calculated to be 4.51 eV, and the newly formed N_2 molecule can be dissociated into the empty region of the six-member ring with an energy barrier of 1.27 eV, recovering a Si-O-Si bridge. The removal of $N(2)_O$ by NO is energetically favorable because the energy of the dissociated N_2 is much lower by 6.60 eV than that of isolated $N(2)_O$ and NO. The interstitial N_2 is an electrically inactive center, with no defect level in the band gap.

Finally, we discuss the electrical improvement of Si oxynitrides, which exhibit a significant reduction of charge traps. Experiments suggested that dominant hole traps in the oxide are attributed to oxygen vacancies.[26] Theoretical calculations[32] also indicated that O vacancies are responsible for the stress-induced leakage current (SILC), while there has been other model involving a complex of O vacancy with hydrogen.[33] The replacement of O vacancies by our inactive N-related complexes in the O-deficient layer will eventually lead to the suppression of the SILC. On the other hand, NH_3-nitrided oxides exhibited a high density of electron traps, which were attributed to $N(2)_O$, while the density of hole traps is lowered.[26,34] When these oxides are thermally reoxidized in O_2, the density of $N(2)_O$ was shown to be greatly reduced,[34] which may result from the deactivation of $N(2)_O$ by reaction with O, based on our calculations. The removal of $N(2)_O$ by O or NO can also explain other experimental findings that the defect densities of $N(2)_O$ are reduced in oxynitrides grown in N_2O or NO ambient, which supplies the source of atomic O or NO. Thus, we suggest that it is an important procedure to supply O or NO interstitials

for suppressing N-related charge traps and enhancing the electrical reliability of oxinitrides.

In conclusion, we find that incorporated N forms the stable defect complex that consists of two N atoms and one O vacancy, especially in Si-rich layers near the Si/SiO_2 interface, where the level of N incorporation is of an order of atomic %. Since this N complex is an electrically inactive center involving O vacancies, the suppression of the electrical activity of O vacancies piled up near the interface would lead to the improvement of the MOS device performance.

We further find that $N(2)_O$ behaving as a charge trap in the the pure oxide can be easily deactivated by reaction with O or NO interstitial, and the subsequent kick-out diffusion of N into the interface leads to the formation of the inactive N complex, suppressing the electrical degradation caused by N incorporation.

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