An analysis of the effect of hydrogen incorporation on electron traps in silicon nitride

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Abstract—The effect of hydrogen incorporation into nitrogen vacancies in silicon nitride on electron trap is analyzed using density functional theory method. A hydrogen atom is attached to a dangling bond which is well separated from other dangling bonds, whereas it is not attached to ones which strongly interact because of lattice distortion. An electron trap level caused by nitrogen vacancy becomes shallow by hydrogen incorporation. An electron is trapped in a deep level created by a silicon dangling bond before hydrogen incorporation, whereas it is trapped in a shallow level created by an anti-bonding state of a silicon-silicon bond after hydrogen incorporation. The simulation results qualitatively explain the experiment in which reduced hydrogen content in silicon nitride shows superior retention characteristics of the programmed state.

I. Introduction

Silicon nitride is widely used as a charge trapping layer in non-volatile memories (NVM)[1]. The retention characteristics of discrete trap NVM is less sensitive to defects in the gate oxide compared to that of floating-gate NVM owing to deep level traps in the charge trapping layer. The deeper the traps, the lower the emission probability from the traps by thermal excitation. Deep traps, therefore, are desired to attain superior retention characteristics.

Enhancement of retention characteristics by reducing hydrogen content in the charge trapping layer is experimentally observed[2]. It is, therefore, of importance to clarify the effect of hydrogen incorporation in silicon nitride from the reliability point of view.

Electron trap level in silicon nitride originates from silicon dangling bonds[3]. Nitrogen vacancy is frequently used in theoretical analysis of the dangling bonds. Previous works[4][5][6][7] using density functional theory (DFT) simulation discussed stability of hydrogen incorporation into the nitrogen vacancy and the electron trap level in silicon nitride assuming absolute zero temperature. The effect of hydrogen on the silicon dangling bond in the temperature range of interest in practical applications has not been fully understood yet.

In this paper, incorporation of hydrogen atom into nitrogen vacancies and its effects on electron trap level are analyzed using DFT simulation. Temperature dependent chemical potential of hydrogen molecule is used in the calculation of hydrogen incorporation energy. The analysis in this paper consists of three steps: (1) formation energy of nitrogen vacancies, (2) incorporation energy of hydrogen into the vacancy, and (3) electron trap level.

II. Modeling

The hexagonal β-Si_3N_4 crystalline phase is considered in this study. The lattice constants are $(a, b, c) = (7.6018, 7.6018, 2.9066)$ Å[8]. A 197-atom supercell obtained by the expansion matrix $2 \times 2 \times 4$ has been considered to describe a diluted defect in the material. At least two different types of nitrogen vacancies are available in β-Si_3N_4 because there are two different types of N atoms in β-Si_3N_4 as shown in Figs. 1[7]. The type 1 nitrogen has two equivalent N-Si bonds and the other bond. The type 2 nitrogen has three equivalent N-Si bonds and, therefore, has threefold symmetry. A primitive cell of β-Si_3N_4 has six N atoms of type 1 and two N atoms of type 2.

Electronic state of a supercell including a point defect is calculated by DFT method[9]. Vanderbilt ultrasoft pseudopotential[10] and Perdew-Burke-Ernzerhof (PBE) functional[11] are used. Electron spin is included with local spin density approximation. The reciprocal space is sampled at Γ-point. Kinetic energy cutoffs for wavefunctions and charge density are $20\,\mathrm{Ry}$ and $200\,\mathrm{Ry}$, respectively. The equilibrium structure is determined by using quasi-Newton algorithm with convergence threshold on forces set to $10^{-3}\,\mathrm{Ry/Bohr}$.

The formation energy of a defect in charge state q is defined as $E_{\mathrm{form}}[S^q] = E_{\mathrm{tot}}[S^q] - \{E_{\mathrm{tot}}[\mathrm{SiN,bulk}] + \sum_i n_i \mu_i - q E_{\mathrm{f}}\} + E_{\mathrm{corr}}$[12], where $E_{\mathrm{tot}}[S^q]$ is the total energy for the super cell S containing the defect, $E_{\mathrm{tot}}[\mathrm{SiN,bulk}]$ is the total energy for the equivalent supercell consisting solely of bulk SiN, n_i is the number of atoms of type i that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell, μ_i is the chemical potential of atoms of type i, E_{f} is the Fermi level, $E_{\mathrm{corr}} = (e^2/4\pi\epsilon_0)(9q^2/10\epsilon_{\mathrm{r}}r_{\mathrm{c}})$ is the background charge correction [13], and r_{c} is the radius of a circle which has the same volume of the supercell. The dielectric constant ϵ_{r} is calculated by DFT simulation. Defects with a low formation energy will be likely to be formed, since less energy needs to be expended in their creation[12].

The incorporation energy E_{inc} of an atom X is defined as the total energy difference before and after the incorporation of the atom[6] $E_{\mathrm{inc}}[X] = E_{\mathrm{tot}}[SX] - (E_{\mathrm{tot}}[S] + \mu_X)$[6], where $E_{\mathrm{tot}}[S]$ and $E_{\mathrm{tot}}[SX]$ are the total energies of the supercell S before and after the incorporation of the atom X, and μ_X is the chemical potential of the atom X. If it is negative, the reaction is exothermic and likely to occur.

The chemical potential μ_X depends on the experimental conditions. It is, however, possible to place bounds on the chemical potential which will be useful in interpreting experi-

mental results[12]. The upper limit of the chemical potential of hydrogen atom is given by half of the chemical potential of a hydrogen molecule $\mu_{H_2}/2$ because hydrogen exists in the form of molecule in high concentration limit. As a function of the pressure of the hydrogen molecule P_{H_2} and the temperature T, the chemical potential of hydrogen molecule is given by $\mu_{H_2} = -kT \log(\eta_{el}\,\eta_{trans}\,\eta_{rot}\,\eta_{vibr})$ with the partition functions of the electronic, translational motion, rotational motion, and vibrational motion, $\eta_{el} = \exp(-E_{tot}[H_2]/kT)$, $\eta_{trans} = (kT/P_{H_2})(2\pi mkT/h^2)^{3/2}$, $\eta_{rot} = 8\pi^2 IkT/(\sigma h^2)$, and $\eta_{vibr} = 1/(1 - \exp(-h\nu/kT))$, respectively[14], where $I = m_I r^2$ is the moment of inertia, $m_H = 1.68 \times 10^{-27}$ kg is the mass of hydrogen atom, $m = 2m_H$ is the mass of hydrogen molecule, $m_I = m_H/2$ is the reduced mass, and $\sigma = 2$ is the symmetry number. The total energy $E_{tot}[H_2]$, the bond length $r = 0.752$ Å, and the vibrational frequency $\nu = 129$ THz of hydrogen molecule are calculated by DFT simulation. Pressure-temperature (P-T) diagram for hydrogen incorporation is obtained by the condition $E_{inc} = 0$. Lower pressure or higher temperature reduces the chemical potential of the hydrogen molecule, which raises the incorporation energy to prevent hydrogen incorporation.

Electron trap level is calculated using Janak's theorem[15]. The total energy difference between the charged states 0 and -1 corresponds to the electron trap level. The energy difference is approximated as a mean value of the lowest unoccupied state for the neutral state defect and the highest occupied state for the -1 charge state defect [7][16].

The trap depth is defined as the difference between the energy of the conduction band edge and the trap level. The energy of the conduction band edge is defined as the lowest unoccupied level of the neutral supercell without defects. As the DFT method is prone to underestimate bandgap[17], the trap level need to be corrected to quantitatively compare with experimental data[13]. In this study, however, no correction is made because qualitative evaluation of the trap depth is intended.

III. RESULTS AND DISCUSSION

Formation energy of nitrogen vacancy

Formation energies of three types of nitrogen vacancies, V(t1), V(t2), and V(t2p), are simulated. The vacancies, V(t1) and V(t2), are formed by removing the type 1 and the type 2 nitrogen atoms defined in Fig. 1, respectively. The vacancy V(t2p) is the puckered version of V(t2), in which a silicon atom with a dangling bond is pushed into the 12-atom ring defined in Fig. 1[7]. The puckered version of V(t1) is energetically unstable and goes back spontaneously to the original geometry of V(t1).

The formation energies of three types of nitrogen vacancy V(t1), V(t2), and V(t2p) at neutral charge state are $+4.8$, $+4.7$, and $+5.1$ eV, respectively. Although the formation energy of the vacancies V(t2p) is higher than that of V(t1) or V(t2), all three types are physically reasonable because the difference is not so large.

Removing a nitrogen atom leads to lattice distortion. The atomic geometries with and without nitrogen vacancy are shown in Fig. 2, respectively. Compared with the atomic geometry of the perfect crystal of β-Si$_3$N$_4$(Fig. 2 (a)), the symmetry of the isosceles triangle consisting of three silicon atoms around the type 1 nitrogen atom is conserved in V(t1)(Fig. 2 (b)). The threefold symmetry of the triangle atoms around the type 2 nitrogen atom, on the other hand, is lost in V(t2)(Fig. 2 (c))[18] because of the Jahn-Teller effect[19].

Incorporation energy of hydrogen

The incorporation energies of a hydrogen atom into the nitrogen vacancies V(t1), V(t2), and V(t2p) are simulated. The hydrogen atom is placed in the equilibrium structures of V(t1), V(t2), and V(t2p) and then the structures are relaxed to obtain the hydrogen incorporated defects H(t1), H(t2), and H(t2p), respectively. The hydrogen atom is initially placed at which the removed nitrogen atom is located in the case of H(t1) or H(t2). In the case of H(t2p), the hydrogen atom is initially placed at the tetrahedral position around the pushed silicon atom.

The incorporation energies to form defects H(t1), H(t2), and H(t2p) at $T = 0$ K are -0.1, -0.1, -1.3 eV, respectively. The incorporation energies of H(t1) and H(t2) are higher than than into H(t2p) because silicon dangling bonds in V(t1) and V(t2) strongly interact[20] and incorporation of H distorts the lattice and raises the total energy. The distance between the silicon atoms around the nitrogen vacancy is stretched by more than 0.5 Å in H(t1) and H(t2) as shown in Fig. 2 (e), (f). In H(t2p), the difference is less than 0.1 Å as shown in Fig. 2 (g).

The P-T diagrams of these defects are shown in Fig. 3. The adsorption/desorption means the hydrogen incorporation is energetically favorable/unfavorable, respectively. The diagrams show that H(t1) and H(t2) are not energetically stable at room temperature, whereas H(t2p) is stable up to 900°C. The desorption temperature of H(t2p) is in agreement with the experimental data in which annealing at 900°C causes a substantial reduction of Si-H bond concentration in silicon nitride[21]. The simulation results suggest that H(t2p) represents a Si-H bond which is stable at room temperature.

Electron trap level

The electron trap levels of defects V(t1), V(t2), V(t2p), and H(t2p) are simulated. Defects H(t1) and H(t2) are excluded because they are not energetically stable at room temperature. Charge state $q = -1$, which correspond to programmed state in discrete trap NVM cells, is assumed in the simulation.

Simulated trap levels are shown in Fig. 4. The trap depth of the defect H(t2p) is much shallower than those of V(t1), V(t2), and V(t2p) because an electron is trapped in a shallow level created by an anti-bonding state of a silicon-silicon bond in H(t2p) in contrast to a deep level created by a silicon dangling bond in V(t1), V(t2), and V(t2p). The energy level of the anti-bonding state is higher than that of the silicon dangling bond as schematically shown in Fig. 5[7]. The deep trap level of V(t2p) compared with that of its counterpart H(t2p) qualitatively explains the experimentally observed enhancement of retention characteristics by reducing hydrogen content in the charge trapping layer[2].

IV. CONCLUSION

The effect of hydrogen incorporation into nitrogen vacancies in silicon nitride on electron trap was analyzed using density functional theory method. A hydrogen atom is attached to a dangling bond which is well separated from other dangling bonds, whereas it is not attached to ones which strongly interact because of lattice distortion. In a nitrogen vacancy without hydrogen termination, an electron is trapped in a deep level created by a silicon dangling bond. After hydrogen termination, an electron is trapped in a shallow level created by an anti-bonding state of a silicon-silicon bond. The simulation results qualitatively explain the experiment in which reduced hydrogen content in silicon nitride shows superior retention characteristics of the programmed state.

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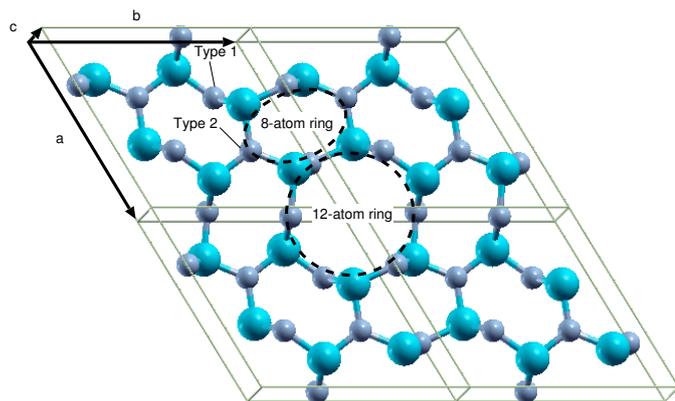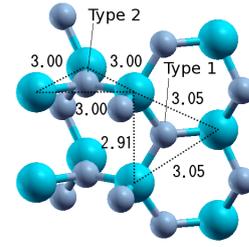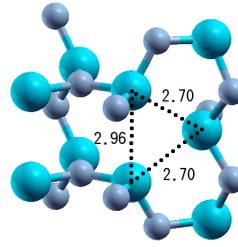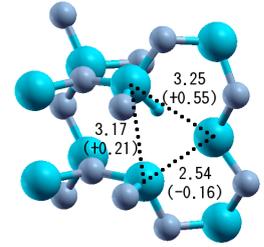[21] H. Jin *et al.*, *J. Electrochem. Soc.*, **153,** G750 (2006).

Fig. 1. The perspective view of primitive cells of β-Si$_3$N$_4$. The supercell with the expansion matrix $2 \times 2 \times 4$ is used in the DFT simulation. A portion of the supercell is shown in this figure for sake of simplicity.
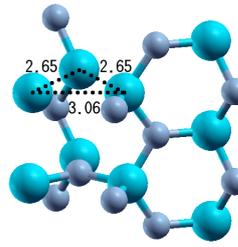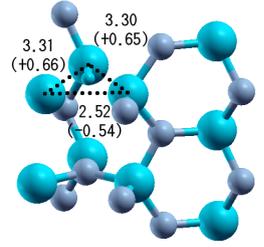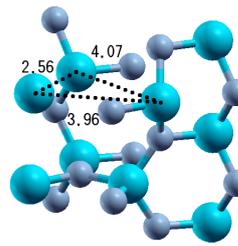

(a) perfect crystal
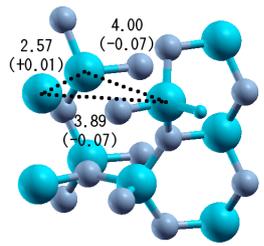
(b) V(t1) (e) H(t1)

(c) V(t2) (f) H(t2)

(d) V(t2p) (g) H(t2p)

Fig. 2. The atomic geometry at neutral charge state. Only atoms around the defect are displayed for clarity. A small blue ball, a medium gray ball, and a large blue ball are hydrogen, nitrogen, and silicon atoms, respectively. 'V' and 'H' mean nitrogen vacancies before and after H incorporation, respectively. 't1', 't2', and 't2p' mean type1, type 2, and type 2 puckered defects, respectively. The vertices of the dotted triangle indicate the centers of the silicon atoms around the nitrogen vacancy. The distance between the silicons is displayed in angstrom. The number in parenthesis is the difference of distances before and after H incorporation.
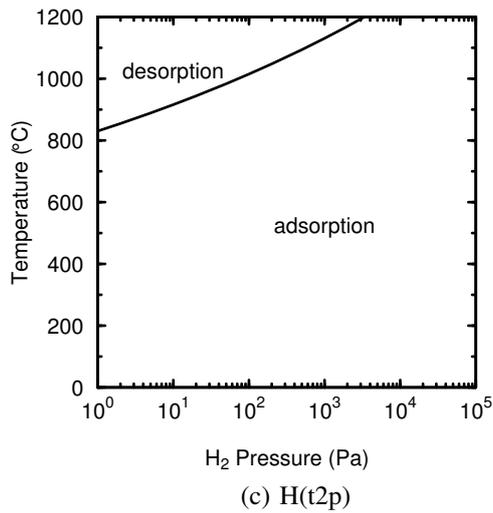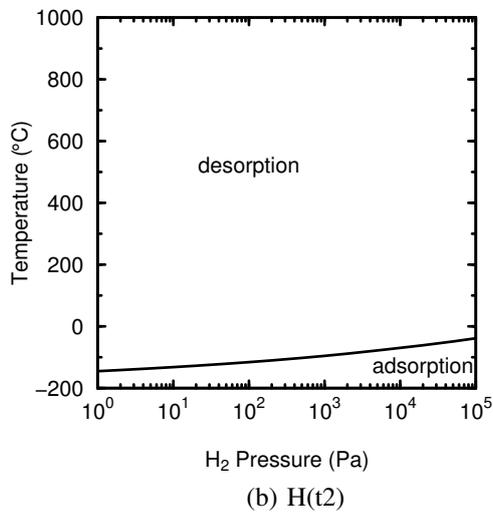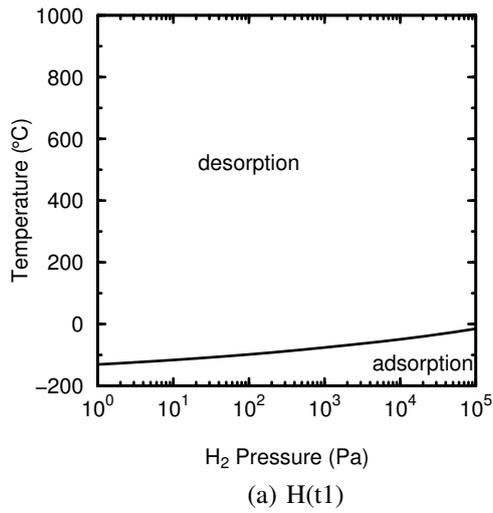
(a) H(t1)

(b) H(t2)

(c) H(t2p)

Fig. 3. The P-T diagram of hydrogen incorporation into nitrogen vacancies. The areas with "adsorption" and "desorption" in the P-T diagram indicate $E_{inc} < 0$ and $E_{inc} > 0$, respectively.
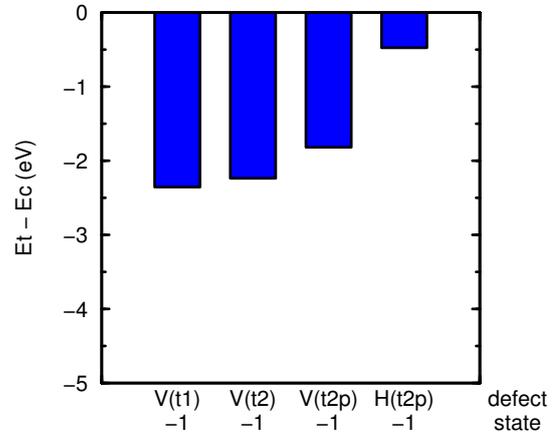

Fig. 4. The electron trap level measured from the conduction band edge at programmed states.
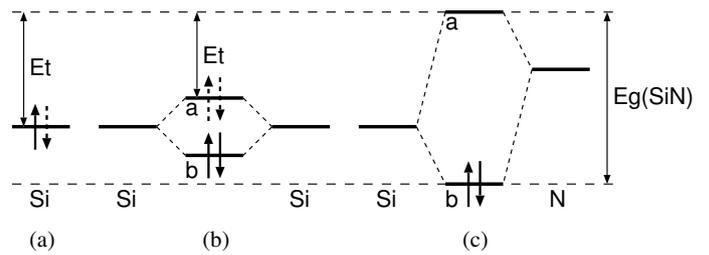

Fig. 5. The schematic diagram of electron trap levels which originate from silicon dangling bond and silicon-silicon bond. The dotted arrows indicate trapped electrons. The labels "b" and "a" mean bonding and anti-bonding orbitals, respectively. (a) silicon dangling bond, (b) silicon-silicon bond, and (c) silicon-nitrogen bond.