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First Principle Study of the Stability of H Atoms in SiN Layers on MONOS-Type Memories During Program/Erase Operations

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Abstract— **Recently, hydrogen has been recognized as an important heteroatom in Metal-Oxide-Nitride-Oxide-Semiconductor (MONOS) -type memories for its quality improvement. However, if stability of H atoms in SiN layers changes by applying high voltage, memory characteristics of MONOS-type memories change during program/erase (P/E) operations, resulting in memory degradation. Therefore, in this paper, we have investigated the stability of H atoms in SiN charge trapping layers of MONOS-type memories during P/E operations by using first principles calculations. Our calculations show that H atoms in Si or N vacancies in SiN layers become unstable and migrate when high voltage is applied, leading to memory degradation with changes of memory characteristics. This result clearly indicates that suppression of H atoms in SiN layers is necessary for realization of high quality MONOS-type memories.**

Keywords-component; MONOS, non-volatile memory, SiN, first principles calculations

I. INTRODUCTION

Metal-Oxide-Nitride-Oxide-Semiconductor (MONOS) -type memories have attracted a great attention for their potential as a highly scalability [1]. One of merits of such memories is that they can trap charges inside very small atomistic regions such as defect sites in SiN layers, leading to the downsizing of nonvolatile memories. Recently, hydrogen has been recognized as an important heteroatom in MONOS-type memories for its quality improvement [2,3]. In the conventional fabrication processes, it has been experimentally observed that H atoms are incorporated into the SiN layer [1]. It has been investigated that stability of H atoms and behaviors of H-incorporated defects as charge traps in a SiN layer. Until now, that H atoms in SiN layers are stable in the neutral charged states and H-incorporated defects in SiN layers can trap charges have been theoretically reported.

However, very high voltage applies to a SiN layer during program/erase (P/E) operations, resulting in changing the stability of H atoms. Indeed, the H-atom migration on the stimulation by energetic charge irradiation is experimentally observed in SiN films [4]. This migration of H atoms in SiN layers has possibility of causing memory degradation of MONOS-type memories with changes of memory characteristics.

Therefore, in this paper, we have theoretically investigated changes of stability of H atoms in a SiN layer by applying a high voltage during P/E operations on the basis of the first principles calculations.

II. CALCULATION METHOD

A. Method of first principle calculation

In this study, total-energy electronic-structure calculations were performed in the framework of density functional theory [5]. The codes used in the present work are from the Tokyo Ab-initio Program Package (TAPP) [6]. We used the Perdew–Burke–Enzerhof generalized gradient approximation [7] for the exchange-correlation energy of interacting electrons. Core-valence interactions were described by ultra-soft pseudo-potentials [8]. Valence wave functions were expanded in a plane-wave basis set with a cutoff energy of 36 Ry. In geometry optimization, all atoms were relaxed until the residual forces become less than 5 mRy/Å. Two irreducible k-points were sampled in the Brillouin zone. We had checked that the present calculation errors of relative energy differences are less than 0.02 eV for typical relaxation energies.

B. Calculation model

We focus on the two types of H atoms in a SiN layer: one is a H atom in a N vacancy forming Si-H bonds. The other is H atoms in a Si vacancy forming N-H bonds. Thus, defect models are considered: a N vacancy and a Si vacancy models. As a bulk phase, we prepared an 84-atom super-cell of β-Si_3N_4, a rectangular parallelepiped whose side lengths are 7.608 Å, 13.177 Å and 8.733 Å respectively. We added one H atom to a N vacancy model and H atoms one to four to a Si vacancy model to correspond to H-incorporation into the SiN layer (Fig. 1). The P/E operations were simulated by injecting electrons (holes) into defects.

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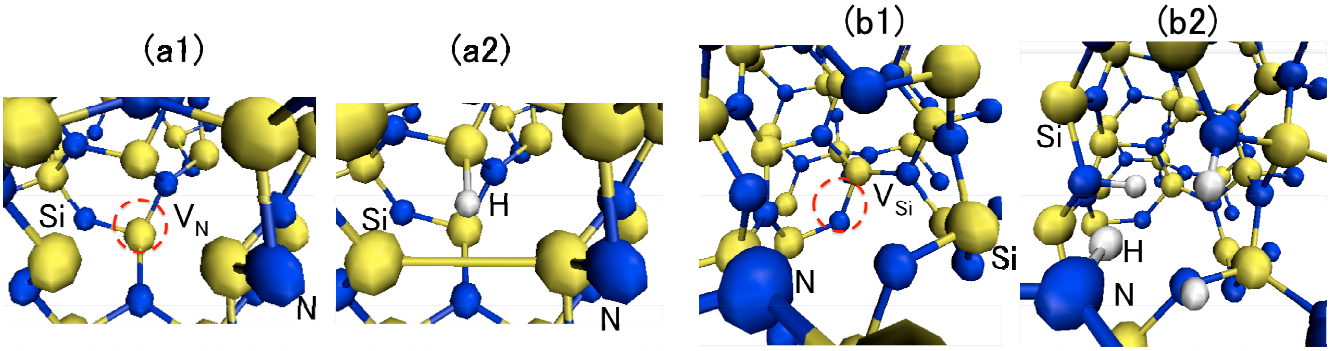

Fig. 1: Calculation models of H-incorporation defects. (a1) N vacancy model. (a2) Most stable structure of a N vacancy with one H atom. (b1) Si vacancy model. (b2) Most stable structure of a Si vacancy with four H atoms. We added one to four H atoms.

C. *Calculations of Formation Energy*

To investigate stable charged states for the present systems, we calculated formation energy (E_{form}) [3]. This is defined as a difference in total energy between systems *A* and *B*. The system *A* comprises a crystal with defects in the neutral charge state and the bulk in charge state *q*, while the system *B* consists of a crystal with defects in charge state *q* and the bulk in the neutral charge state.

Mathematically, the formation energy can be expressed by

$$E_{\text{form}} = (\text{Total Energy of B}) - (\text{Total Energy of A})$$
$$= [E_{defect}(q) + E_{bulk}(0)] - [E_{defect}(0) + E_{bulk}(q)]$$
$$+ \frac{3q^2}{10\varepsilon r_0} + \begin{cases} qE_F & q > 0 \\ qE_F - E_{gap} & q > 0 \end{cases} \quad (1)$$

$E_{defect}(q)$ is the total energy of crystal with defects in charge state *q*, and $E_{bulk}(q)$ is the total energy of bulk crystal in charge state *q*. E_F and E_{gap} indicate Fermi energy and band gap in bulk crystal, respectively. $3q^2/(10\ \varepsilon\ r_0)$ is a background charge correction proposed by Blöchel [9], where ε is the relative permittivity and r_0 is the radius of a sphere which corresponds to the same volume as the supercell using in the calculations. Plotting E_F in a range of the band gap of Si_3N_4 bulk crystal, the lowest value at each Fermi energy indicates the stable charge state for system with defects.

D. *Estimation method of stability of H atoms*

For investigation of the changes of stability of H atoms during P/E operation, charged state dependent formation energies of H-incorporated defects are compared with the formation energies of defects without H atoms. The stability of H atoms in a N or Si vacancy are compared with H_2 molecules. We define $E_{\text{formW/O H}}$ as a following equation.

$$E_{formW/OH} = E_{Vform} + \frac{n}{2} E_{H2} \quad (2)$$

where E_{Vform} is the formation energy of the systems containing only one N vacancy or one Si vacancy, and E_{H2} is the total energy of molecular hydrogen. *n* indicates the number of H atoms in the systems. If $E_{\text{formW/O H}}$ is less than formation energy of the system containing N or Si vacancy with H atoms, H atoms in Si vacancy or N vacancy are unstable more than H molecules.

III. Results and Discussions

A. *H atoms in N vacancies*

First, we describe calculation results of stability of H atoms in N vacancies. The formation energy diagram of N vacancy model is plotted in Figure 2. In this diagram, the defect type and charged state with lowest energy is most stable state at each Fermi energy. In this model, stable charged states and position of H atoms are q=0 and +2 of a N vacancy with a H atom model and q=+1 and –1 of a N vacancy without H atoms model. A H atom in a N vacancy in neutral charged state is more stable than H_2 molecules when Fermi energy is in the middle of bandgap of Si_3N_4. However, when Fermi energy is located close to the valence band top or the conduction band bottom of Si_3N_4, H_2 molecules with a intrinsic N vacancy in q=–1 or +1 are more stable than a H atom in a N vacancy. This result shows that stability of H atoms changes during P/E operation in N vacancy models.

Figure 3 shows the atomistic structures of a neutrally charged (q=0) N vacancy model with one H atom and negatively (q=–1), neutral (q=0), and positively (q=+1) charged N vacancy models without H atoms. In case of a neutrally charged N vacancy with a H atom, the H atom terminates one Si dangling bond and two Si atoms make a new Si-Si bond. However, when Fermi energy is located close to the valence band top or the conduction band bottom of Si_3N_4, which corresponds to the situation, where a high electric field is applied, H_2 is more stable than H atoms in N vacancies. These results clearly indicate that H atoms in N vacancies in SiN layers have the possibility to migrate during P/E operations, leading to memory degradations of MONOS-type memories with changes of memory characteristics.

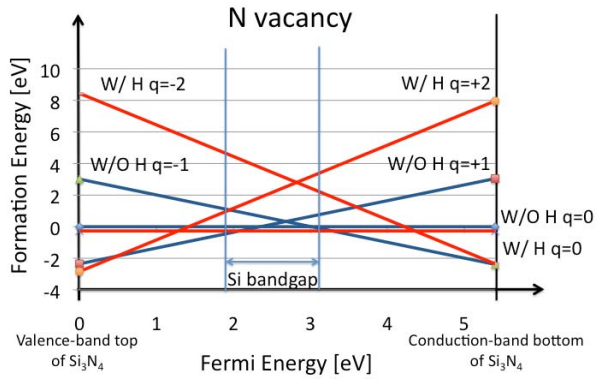

Fig. 2: Formation energy diagrams of the defects with and without H atoms in a N vacancy model. A H atom is more stable than H_2 molecules when Fermi energy is located in the middle of bandgap of Si_3N_4. However, H atom becomes unstable when Fermi energy is close to the valence band top and the conduction band bottom.

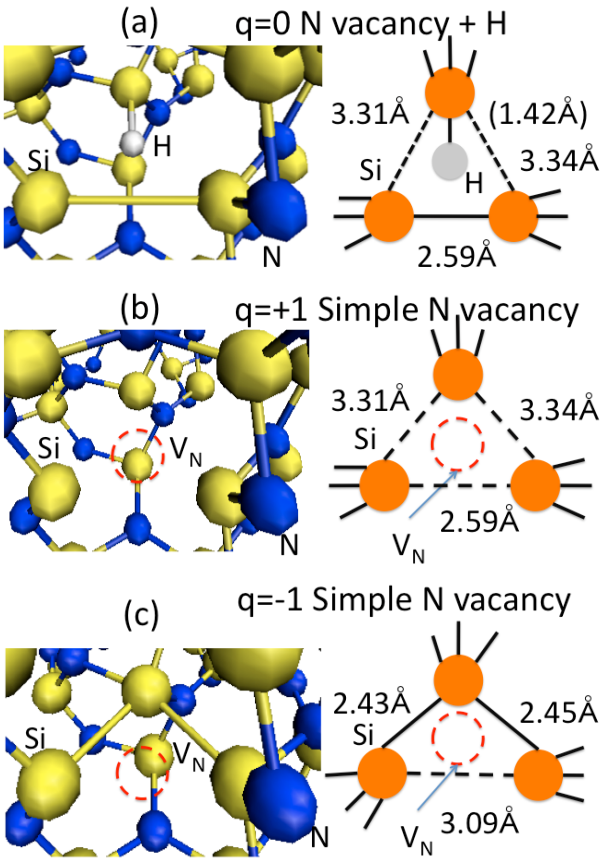

Fig. 3: Atomistic structures of N vacancy models and their schematic views. (a) a N vacancy with a H atom in the q=0 charged state (b) a N vacancy without H atoms in q=+1 charged states. (c) a N vacancy without H atoms in q=−1 charged states.

B. H atoms in Si vacancies

Next, we describe the calculation results about stability of H atoms in a Si vacancy in SiN layers. Calculation results of formation energies of Si vacancy models are plotted in Figure 4. As well as the N vacancy model, Figure 4 shows that stability of H atoms changes during P/E operation in the Si vacancy model.

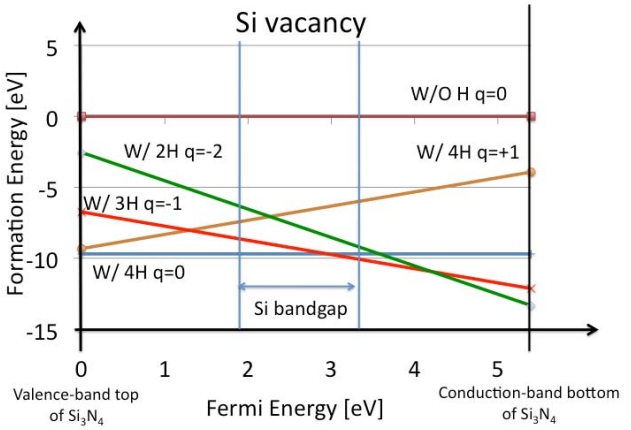

Fig. 4: Formation energy diagrams of the defects with and without H atoms in a Si vacancy model. H atoms in Si vacancy are likely to be removed from a Si vacancy due to its unstable feature when Fermi energy is close to the conduction band bottom.

In a Si vacancy models, the formation energy of four H atoms, all Si dangling bonds are terminated by H atoms, in neutral charged state is the lowest when Fermi energy is located in the middle of bandgap of Si_3N_4. However, when Fermi energy is close to the conduction band bottom of Si_3N_4, corresponding to P/E operations, the formation energy of a Si vacancy with three H atoms model in q=−1 or a Si vacancy with two H atoms model in q=−2 is the lowest. Figure 5 shows the atomistic structures of a neutral Si vacancy with four H atoms, a Si vacancy with three H atoms in the q=−1 charged state and a Si vacancy with two H atoms in the q=−2 charged state. These results indicate that when electric field is not applied, H atoms in a Si vacancy can terminate all N dangling bonds. However, when Fermi energy is close to the conduction band bottom of Si_3N_4, which is the situation under a high electric field, H atoms cannot terminate all N dangling bonds of the Si vacancy.

The above calculations show that P/E operations cause changes of stability of H atoms and in SiN charge trapping layers of MONOS type memories, causing migration of H atoms. These results provide a natural explanation for recent experimental results [4]. This movement of H atoms causes changes of memory characteristics of H-incorporated defects, which can leads to the memory degradation of MONOS-type memories.

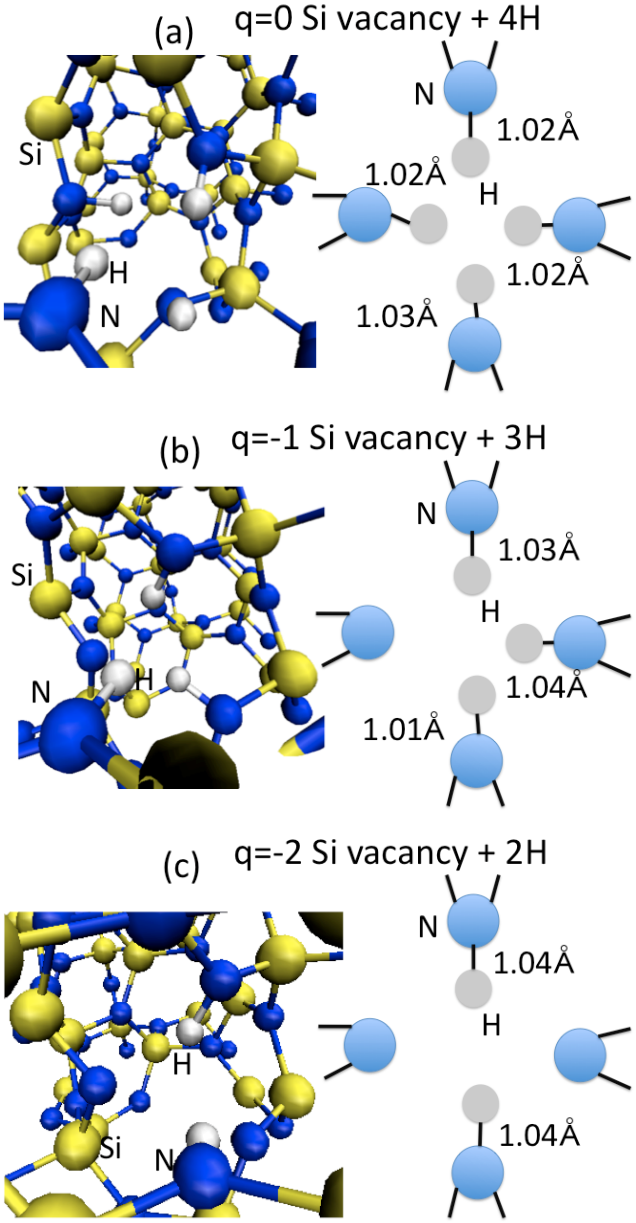

Fig. 5: Atomistic structures of Si vacancy models and their schematic illustrations. (a) a Si vacancy with four H atoms in the q=0 charged state. In this structure, H atoms terminate all Si dangling bonds. (b) a Si vacancy with three H atoms in q=-1 charged states. (c) a Si vacancy with H atoms in q=-2 charged states.

IV. Conclusion

In this paper, we theoretically investigated stability of H atoms in SiN layers on MONOS-type memories during P/E operations on the basis of the first principles calculations. We focus on the two types of H atoms in SiN layers. One is a H atom which terminates a Si dangling bonds, the other is a H atom which terminates a N dangling bond. Our calculations indicate that both H atoms in N and Si vacancies become unstable when a high voltage is applied, leading to memory degradation with changes of memory characteristics. This result clearly indicates that suppression of H atoms in SiN layers is necessary for realization of high quality MONOS-type memories.

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References

[1] M. Ishiduki , Y. Fukuzumi, R. Katsumata, M. Kito, M. Kido, H. Tanaka, Y. Komori, Y. Nagata, T. Fujiwara, T. Maeda, Y. Mikajiri, S. Oota, M. Honda, Y. Iwata, R. Kirisawa, H. Aochi and A. Nitayama, "Optimal Device Structure for Pipe-shaped BiCS Flash Memory for Ultra High Density Storage Device with Excellent Performance and Reliability," Tech Dig. International Electron Devices Meeting 2009, on Baltimore, MD, USA, pp.625-628, Dec. 2009

[2] E. Vianello, L. Perniolaa, P. Blaisea, G. Molasa, J. P. Colonnaa, F. Driussib, P. Palestrib, D. Essenib, L. Selmib,N. Rochata, C. Licitraa, D. Lafonda, R. Kiesa, G. Reimbolda, B. De Salvoa and F. Boulangera, "New insight on the charge trapping mechanisms of SiN–based memory by atomistic simulations and electrical modeling," Tech Dig. International Electron Devices Meeting 2010, on Baltimore, MD, USA, pp.83-86, Dec. 2009

[3] A. Otake, K. Yamaguchi, K. Kamiya, Y. Shigeta, K. Shiraishi, "An atomistic study on hydrogenation effects toward quality improvement of program/erase cycle of MONOS-type memory" IEICE Transactions,Vol.E94-C, No.5, 2011

[4] Z. Liu, S. Ito, S. Hiroshima, S. Koyama, M. Makabe, M. Wilde, K. Fukutani, "Mobile and stable hydrogen species in the interface layer between poly silicon and gate oxynitride," Tech Dig. 2010 International Reliability Physics Symposium (IRPS) 2010, on Anaheim, CA,USA, p.417-423, May 2010.

[5] W. Kohn and L.J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effect," Phys. Rev. vol.140, pp.A1133-1138, November 1965.

[6] J. Yamauchi and M. Tsukada, "First-principles study on energetics of c-BN(001) reconstructed surfaces," Phys. Rev. B, vol.54, no.8, pp.5586-5603, August 1996.

[7] J. P. Perdew, Kieron Burke, Matthias Ernzerhof, "Generalized Gradient Approximation Made Simple," Phys. Rev. Lett. vol.77, no.18, pp.3865-3868, October 1996.

[8] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," Phys. Rev. B, vol.41, no.11 pp.7892-7895, April 1990.

[9] P.E. Blochl, "First-principles calculations of defects in oxygen- deficient silica exposed to hydrogen," Phys. Rev. B, vol.62, no.10, pp.6158-6179, September 2000.