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Mechanisms of Nitrogen Segregation and Hole Trap Generation at the Interface of SiO₂/Si(100)

Takahiro Yamasaki and Chioko Kaneta

Fujitsu Laboratories Limited

10-1 Morinosato-Wakamiya, Atsugi, 243-0197, Japan

Phone/Fax: +81-46-250-8235/+81-46-250-8804, E-mail: t.yamasaki@jp.fujitsu.com

1. Introduction

In the fabrication processes of MOS devices with very thin gate insulators of SiO₂, N atoms are introduced in the SiO₂ region to improve device characteristics by using various nitridation processes, e.g. thermal annealing in NO or N₂O gas ambients and remote plasma nitridation. By thermal nitridation, N atoms are incorporated in the region near the SiO₂/Si interface and are coordinated to three or two Si atoms [1]. Control of concentration, position and coordination of N atoms is very crucial, because enough amount of incorporated N atoms to prevent penetration of boron atoms from the p⁺-gate may degrade reliability of devices due to negative bias temperature instability (NBTI). Several researchers ascribed the acceleration of NBTI by the nitridation to some reaction between N atoms and water related materials in the SiO₂ layer near the interface [2]. However, we have not yet reached a consensus. Bonding characteristics of N atoms in the SiO₂ region should be clarified to understand the mechanisms of N incorporation under nitridation process and of reliability degradation. In this paper we investigate stabilities and electronic states of variety of three- and two-coordinated-N-configurations near the SiO₂/Si(100) interface to understand segregation of the N atoms at the interface and the degradation with hole trap site generation.

2. Methodology

A calculation method we have used here is the first principles molecular dynamics method based on the density functional theory and employing pseudopotentials. Pseudopotentials of O 2p, N 2p and H 1s orbitals are non-norm conserving Vanderbilt type [3] and others are norm conserving. Cut off energies for plane wave expansion of wave functions and charge densities are 25 and 144 Ry, respectively. For exchange-correlation potential, we added a generalized-gradient-approximation-correction [4] to the local density term. A repeated slab model is used to simulate interface structures. Two kinds of abrupt and perfect SiO₂/Si(100) interface structures, i.e. tridymite- and quartz-SiO₂/Si models [5], are used to form Si₂=N• and Si₂H=N configurations by substituting an N atom or an H-terminated N atom for an O atom in the models. Here, • denotes a dangling bond. Other matrices are interface defect structures of Si-dangling bonds without or with backbond oxygen (SDB0, SDB1) [6] (Fig. 1), which are modeled by modifying the structure of the tridymite-SiO₂/Si model. We

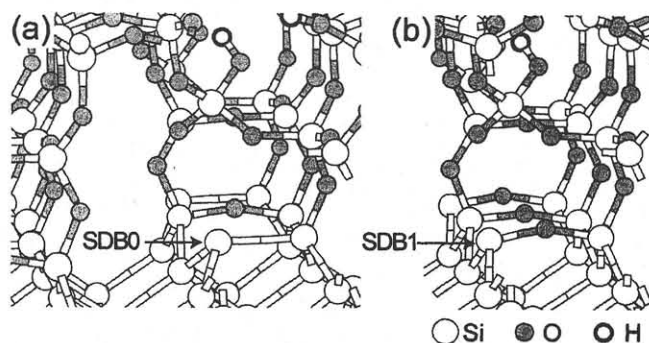


Fig.1. Two SiO₂/Si models with interface defects. SDB0 and SDB1 indicated by arrows in (a) and (b) are the Si atoms each of which has a dangling bond. SDB1 has a backbond O atom, but SDB0 does not have.

substituted an N atom for a Si atom of these matrices to form three-coordinated N configurations of Si₃=N, Si₂O=N and O₃=N. The interface Si(100) unit cells are 2x2 and $\sqrt{2} \times \sqrt{2}$ for the tridymite- and the quartz-SiO₂/Si models, respectively.

3. Results and Discussion

We have optimized four kinds of Si₂=N• and their H-terminated configurations. We label the Si₂=N• configurations as shown in Fig. 2. Substitution of an N atom for an O atom hardly changes surrounding atomic positions. The Si₂=N• at the interface ((T|Q)-a) is the most stable, and Si₂=N• becomes less stable as it goes far from the interface. Here ((T|Q)-a) denotes (T-a) or (T-b). Relative energies of

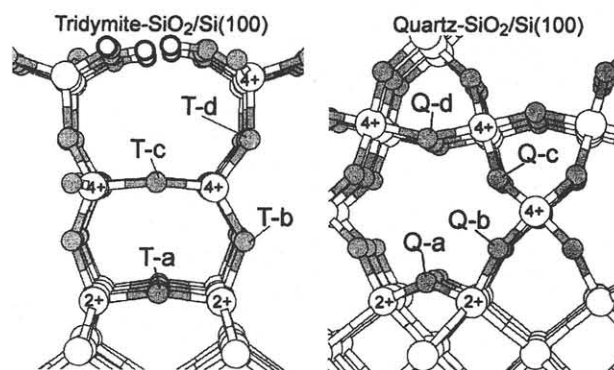


Fig. 2. Labels of the O sites which are substituted by an N atom to form Si₂=N• configurations in the tridymite-SiO₂/Si (left hand side) and in the quartz-SiO₂/Si (right hand side) interface structures. "2+" and "4+" on Si atoms denote anion numbers which coordinate to the Si.

(T-b), (T-c) and (T-d) to (T-a) are +0.38, +1.00 and +1.05 eV, respectively, and those of (Q-b), (Q-c) and (Q-d) to (Q-a) are +0.51, +1.19, and +1.01 eV, respectively. These $\text{Si}_2=\text{N}^\bullet$ configurations are classified by the bonding Si atoms as ((T|Q)-a) $\text{Si}^{2+}-\text{N}-\text{Si}^{2+}$, ((T|Q)-b) $\text{Si}^{2+}-\text{N}-\text{Si}^{4+}$, and ((T|Q)-c and (T|Q)-d) $\text{Si}^{4+}-\text{N}-\text{Si}^{4+}$, where superscripts correspond to the numbers of bonding anions to the Si atoms. According to these results, we can assume that a $\text{Si}_2=\text{N}^\bullet$ around the interface have a tendency to move in to the interface by thermal annealing. An $\text{Si}^{1+}-\text{N}-\text{Si}^{2+}$ coordination that can be generated by insertion of an N atom into an Si-Si bond in the substrate near the interface is not stable because of accumulated stress to the bonding Si atoms, but could be stabilized if the stress were released enough. $\text{Si}_2=\text{N}^\bullet$ configurations have gap states which trap holes. Terminating the dangling bond with an H atom eliminates the gap state. We have estimated dissociation energies of H atoms in the $\text{Si}_2\text{H}=\text{N}$ configurations, which are shown in Fig. 3. Interface $\text{Si}_2\text{H}=\text{N}$ configurations have smaller H-N dissociation energies. $\text{Si}_2\text{H}=\text{N}$ becomes stable as it goes deeper in the SiO_2 region. The dominant reason is because Si-N-Si bond angles after H-termination can be easily relaxed in the deeper SiO_2 region than at the interfaces.

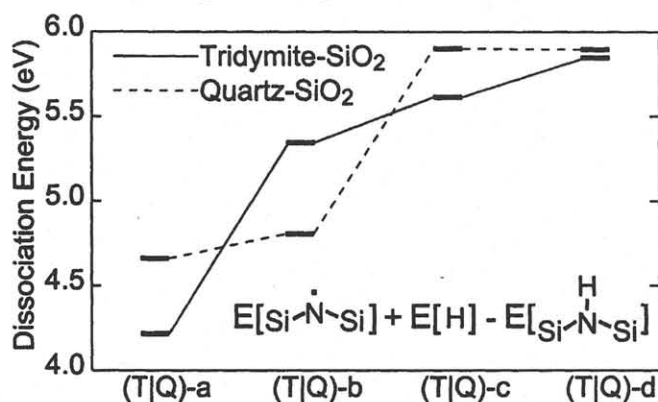


Fig. 3. H-N dissociation energies of $\text{Si}_2\text{H}=\text{N}$ configurations. H energy $E[\text{H}]$ is taken from the value of H in a $\text{Si}_2\text{N}_2\text{O}$ crystal.

Next, we have optimized three $\text{Si}_3=\text{N}$, one $\text{Si}_2\text{O}=\text{N}$ and one $\text{O}_3=\text{N}$ configurations as shown in Fig. 4. The $\text{O}_3=\text{N}$ configuration (d) is very unstable compared to others, e.g. to the configuration (a) by 7.7 eV. The $\text{Si}_3=\text{N}$ configurations are more stable compared to the $\text{Si}_2\text{O}=\text{N}$ (a') by 0.6-2.4 eV. Among three $\text{Si}_3=\text{N}$ configurations, the interface $\text{Si}_3=\text{N}$ (a) is the most stable, followed in order by the second layer $\text{Si}_3=\text{N}$ (b) and the third layer $\text{Si}_3=\text{N}$ (c). The interface $\text{Si}_3=\text{N}$ configuration of (a) has no gap states. Substituted N atoms in the configurations (b) and (c) generate dangling bonds at the Si atoms near the N atoms, and the dangling bonds create gap states and work as hole trapping sites. Termination of a dangling bond with an H atom eliminates the gap state. The N atoms around the interface would be stabilized and have no gap states by substituting for SDB0's and forming $\text{Si}_3=\text{N}$ if they exist around.

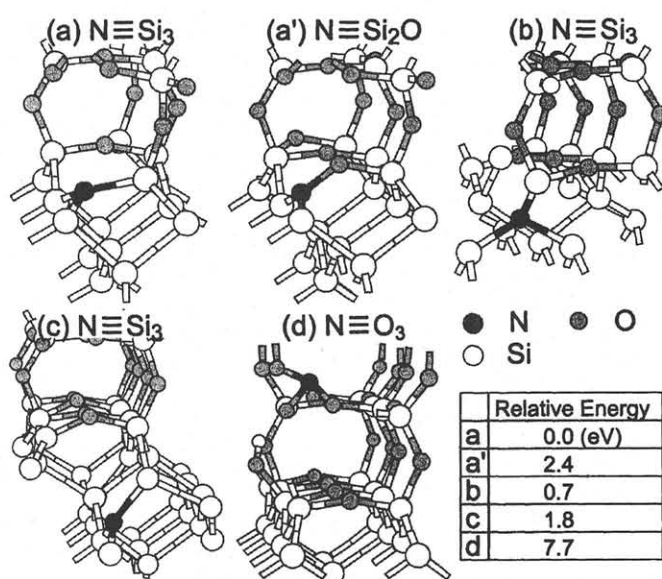


Fig. 4. Three-coordinated-N-configurations. ((a) $\text{Si}_3=\text{N}$ at the interface where N is substituted with SDB0, (a') $\text{Si}_2\text{O}=\text{N}$ at the interface where N is substituted for SDB1, (b) $\text{Si}_3=\text{N}$ at the second layer in the substrate, (c) $\text{Si}_3=\text{N}$ at the third layer in the substrate, and (d) $\text{O}_3=\text{N}$ in the SiO_2 region

4. Summary

When incorporated N atoms come to near the interface through the SiO_2 layer, they would prefer energetically to form a $\text{Si}_2=\text{N}^\bullet$ configuration at the interface. By annealing, these N would be more stabilized by substituting for SDB0's if they exist around, or may be stabilized by reconfiguring surrounding networks to form a $\text{Si}_3=\text{N}$. Other $\text{Si}_2=\text{N}^\bullet$ configuration would be stabilized by terminating their dangling bonds with H atoms. However interface $\text{Si}_2=\text{N}-\text{H}$ configurations have weaker N-H bonding energies. These H atoms may be dissociated with relatively smaller activation energies and will leave $\text{Si}_2=\text{N}^\bullet$, which have gap states for hole trapping.

References

- (1) R. I. Hegde, B. Maiti, and P. J. Tobin, *J. Electrochem. Soc.* **144** (1997) 1081.
- (2) N. Kimizuka, K. Yamaguchi, K. Imai, T. Iizuka, C. T. Liu, R. C. Keller, and T. Horiuchi, *Symp. on VLSI Technol.*, (2000) 92.
- (3) D. Vanderbilt, *Phys. Rev. B* **41** (1990) 7892.
- (4) J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991)
- (5) T. Yamasaki, C. Kaneta, T. Uchiyama, T. Uda, and K. Terakura, *Phys. Rev. B* **63** (2001) 115314.
- (6) C. Kaneta, T. Yamasaki, T. Uchiyama, T. Uda, and K. Terakura, *Microelectronic Engineering* **48** (1999) 117.