

# Stabilities and Electronic States of Incorporated Nitrogen Atoms at the Interface of SiO<sub>2</sub>/Si(100)

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In the fabrication processes of MOS devices with very thin gate insulators of SiO<sub>2</sub>, N atoms are introduced into the SiO<sub>2</sub> region to improve device characteristics. The control of concentration, position and coordination of N atoms is very crucial to cope with both prevention of B penetration and suppression of degradation due to the negative bias temperature instability (NBTI). Acceleration of NBTI by the nitridation may be attributed to some reaction concerned with water related materials in the SiO<sub>2</sub> layer near the interface, which were proposed for the SiO<sub>2</sub>/Si interface without nitridation [1]. However, a consensus is not reached. We have investigated stabilities and electronic states for variety of three- and two-coordinated-N-configurations near the SiO<sub>2</sub>/Si(100) interface to understand the mechanisms of the segregation of N atoms at the interface and of the degradation with hole trap site generation. The method we have used is the first-principles molecular-dynamics method based on the density functional theory and employing pseudopotentials.

Two perfect SiO<sub>2</sub>/Si interface structures, i.e. tridymite- and quartz-SiO<sub>2</sub>/Si models [2], are prepared to form Si<sub>2</sub>=N• and Si<sub>2</sub>H≡N configurations by substituting an N atom or an N-H for an O atom in the models. Here, • denotes a dangling bond. The substitution of an N atom for an O atom hardly changes surrounding atomic positions. Si<sub>2</sub>=N• configurations at the interface are the most stable, and Si<sub>2</sub>=N• becomes less stable as it goes far from the interface (Fig. 1). We can assume from these results that a Si<sub>2</sub>=N• around the interface have a tendency to move in to the interface by thermal annealing. Si<sub>2</sub>=N• configurations cause gap states, which trap an electron or a hole depending on the Fermi energy level. Termination of the dangling bond with an H atom eliminates the gap state. We have, then, estimated dissociation energies of H atoms in the Si<sub>2</sub>H≡N configurations (Fig. 2). Interface Si<sub>2</sub>H≡N configurations have smaller H-N dissociation energies. Si<sub>2</sub>H≡N becomes stable as it goes deeper in the SiO<sub>2</sub> region.

We have also optimized three Si<sub>3</sub>≡N, one Si<sub>2</sub>O≡N and one O<sub>3</sub>≡N configurations. Matrices for these configurations are interface defect structures with an Si atom having a dangling-bond [3], which are modeled by modifying the tridymite-SiO<sub>2</sub>/Si structure. The Si<sub>3</sub>≡N configurations are more stable compared to the Si<sub>2</sub>O≡N by 0.6-2.4 eV. Among three Si<sub>3</sub>≡N, the interface Si<sub>3</sub>≡N is the most stable, and it has no gap states. Other Si<sub>3</sub>≡N configurations generate dangling bonds at Si atoms near the N atom, which originate gap states and work as hole trapping sites. Termination of a dangling bond with an H atom eliminates the gap states.

We can figure out mechanisms of the segregation of N atoms and of trap site generation. When incorporated N atoms come to near the interface through the SiO<sub>2</sub> layer, they prefer energetically to form Si<sub>2</sub>=N• configurations at the interface. Dangling bonds in the Si<sub>2</sub>=N• configurations can be eliminated with H atoms. H atoms in the interface Si<sub>2</sub>=N-H configurations dissociate with relatively smaller activation energies compared to

other Si<sub>2</sub>=N-H in the SiO<sub>2</sub>. The dissociation of the H atoms generates the gap states that work as hole or electron trapping sites depending on the Fermi energy level. By annealing, the interface Si<sub>2</sub>=N• configurations will be more stabilized by substituting the N atom for an interface dangling-bond-Si atom if it exists around, or for one of substrate Si atoms. The Si<sub>3</sub>≡N configurations occurred in the substrate region, however, generate hole trapping sites in the Si atoms near the N atoms. Plausible N configurations that accelerate NBTI are these Si<sub>3</sub>≡N configurations in the substrate close to the interface.

## References

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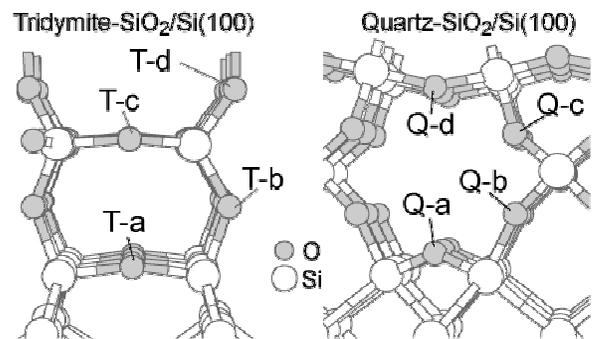


Fig. 1. Labels of the O sites which are substituted by an N atom to form Si<sub>2</sub>=N• configurations in the tridymite-SiO<sub>2</sub>/Si (left) and in the quartz-SiO<sub>2</sub>/Si (right) interface structures. Relative energies of (T-b), (T-c) and (T-d) to (T-a) are +0.38, +1.00 and +1.05 eV, respectively, and those of (Q-b), (Q-c) and (Q-d) to (Q-a) are +0.51, +1.19, and +1.01 eV, respectively.

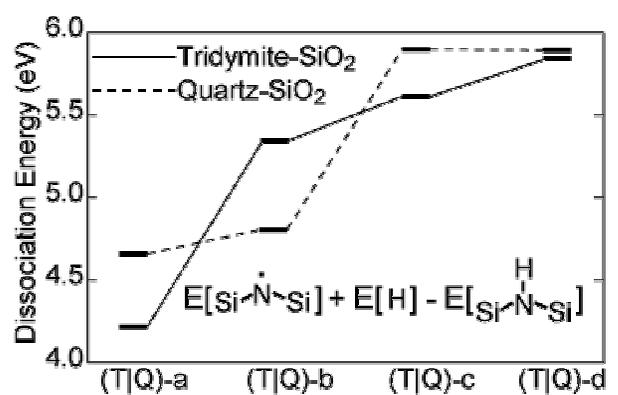


Fig. 2. H-N dissociation energies of Si<sub>2</sub>H≡N configurations. H energy E[H] is taken from the value of H in a Si<sub>2</sub>N<sub>2</sub>O crystal. Here, merely relative energy values among the configurations are meaningful.

