

Molecular Orbital Examination of Negative-Bias Temperature Instability Mechanism

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Abstract

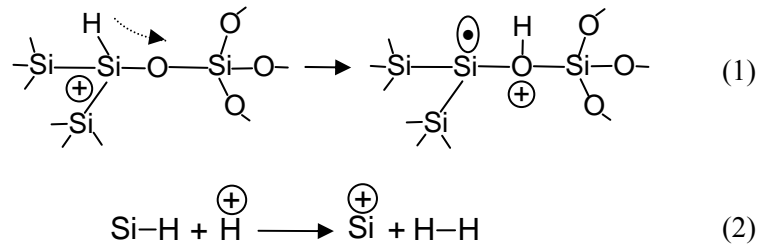
To clarify the microscopic mechanism of Negative-Bias Temperature Instability (NBTI), which is one of serious reliability issues in CMOS technology, the transfer reaction of the positive fixed charge at the Si/SiO₂ interface accompanied by hydrogen migration was investigated using the ab initio molecular orbital method. Comparing the activation energies, we determined the most likely reaction path. We found that the reaction path can be stabilized more by migration of an electrically neutral H atom from a Si substrate to a positively charged O atom than by migration of a proton from a Si substrate to an electrically neutral O atom. The calculated Mulliken atomic charges and atomic spin densities also supported our conclusion.

1 Introduction

Negative-bias temperature instability (NBTI) is becoming one of the serious reliability issues in recent complementary metal-oxide-silicon (CMOS) technology. NBTI usually accompanies positive charge and interface state generation which degrade p-channel MOS devices. Understanding of the microscopic mechanism of NBTI is demanded to design a higher-performance and more reliable device. Though extensive studies have been done, there are still several open questions on NBTI mechanism [1]. We previously reported a NBTI mechanism where a positive-charge transfer accompanies migration of an electrically neutral hydrogen atom (hydrogen-originated reaction; reaction (1))[2].

Another basic reaction (reaction (2)) was reported as the most plausible NBTI mechanism by Tsetseris et al. [3]. They proposed proton-originated reaction (reaction (2)) where a proton in a SiO₂ film depassivates a Si-H bond in a Si substrate to generate a positively charged Pb_0 center.

A positive fixed charge in the reaction (2) transfers from a SiO₂ film to a Si substrate against applied electric field in NBTI. In this paper, we investigated the potential energy surface of the proton-originated reaction (2) in detail by employing molecular-orbital calculations.



2 Calculation Method

The structure of a model used for calculations of potential energy surface is shown in Figure 1. Two molecules, $\text{Si}(\text{SiH}_3)_3$ and $\text{O}(\text{Si}(\text{OH})_3)_2$ are displaced at a distance of 7 Å as models for a Si substrate and a SiO_2 film, respectively. A proton in a SiO_2 film was assumed to be bonded to an oxygen atom in a SiO_2 film at the beginning of the reaction. Two possible paths for a positive charge transfer can be considered (Figure 2). One is a proton-migration path (path 1) and the other is a hydrogen-migration path (path 2). Path 1 can be calculated with the restricted Hartree-Fock (RHF) method while the unrestricted Hartree-Fock (UHF) method is necessary for calculation of path 2. The position of a proton was adopted as a parameter for a potential energy surface. All the calculations were performed using the ab initio molecular-orbital program, Gaussian 03 with 3-21g* basis set [4].

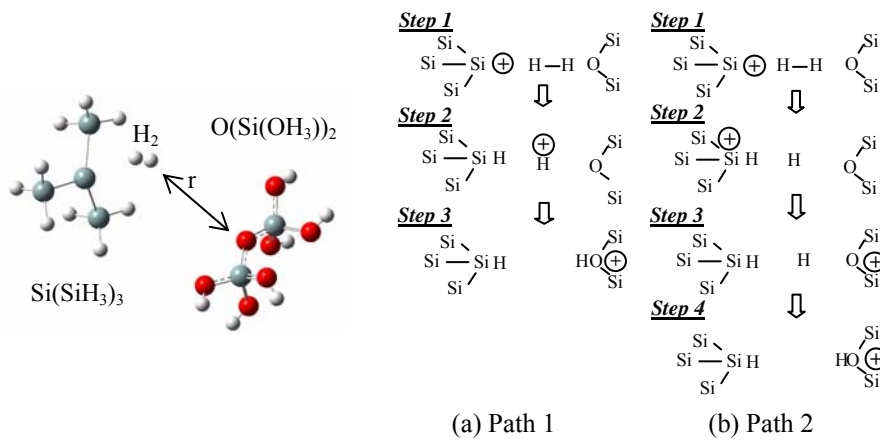


Figure 1: A Si/ SiO_2 interface model with an interstitial H_2 .

Figure 2: Two possible paths of NBTI reaction (2).

3 Results and Discussion

The calculated potential curves are displayed in Fig. 3. The UHF solutions for steps 2 and 3 in path 2 have lower energies than the corresponding RHF solutions.

The energy lowering is about 3 eV at step 2 in path 2 and about 1 eV at step 3 in path 2. This clearly indicates that hydrogen-originated reaction is energetically more favorable than proton-originated reaction. Therefore, a hydrogen atom migrates as an electrically neutral atom, not as a proton, in the transfer reaction of a positive charge at the Si/SiO₂ interface. We display the atomic spin densities for steps 2 and 3 in path 2 in Fig. 4. No spin density appears in steps 1 and 4. In step 2 in path 2 (Fig. 4b), an isolated hydrogen atom that has a spin density of about 1.0 is produced. The corresponding density of opposite spin (hole) appears on the Si atoms in the Si substrate. The other hydrogen atom to form a hydrogen molecule makes a bond with the Si atom trapping a hole in the Si substrate. In step 3 in path 2, the hole transfers from the Si substrate to the O atom in a SiO₂ film and generates a spin density on the O atom of -1.0, while the spin density on the isolated hydrogen atom stays unchanged to be 1.0 (Fig. 4a). These spin densities of opposite signs disappear in step 4 to form a new H-O bond. The appearance of spin density on the hydrogen atom in the intermediate state of the reaction is evidence for hydrogen-originated reaction in NBTI.

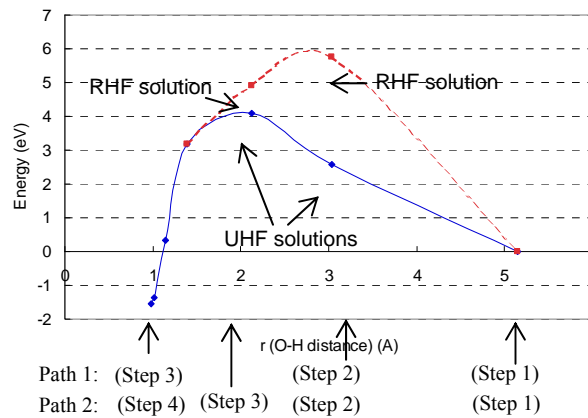


Figure 3 : Potential curves of paths 1 and 2 for a proton-originated NBTI reaction corresponding to Eq. (2).

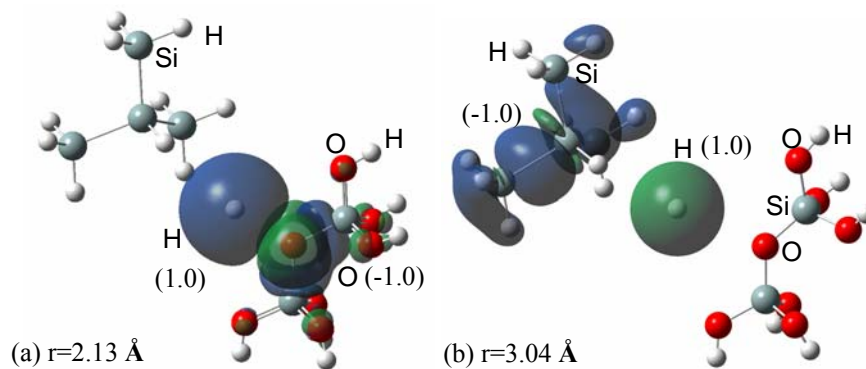


Figure 4 : Isosurface of electron spin density. (a) step 3 in path 2 and (b) step 2 in path 2 . Numbers in the parentheses are atomic spin densities.

Summary

Using the ab initio molecular-orbital method and a molecular model of the Si/SiO₂ interface with an interstitial hydrogen molecule, we investigated the potential energy surface of the proton-originated reaction which was proposed as the most plausible NBTI mechanism. The path that generates an electrically neutral hydrogen is more stable than the path that involves a proton. Consequently, hydrogen migrates as an electrically neutral atom in NBTI, not as a proton.

Acknowledgements

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