

**A-3-2****Interface Structures Generated by Negative-Bias Temperature Instability in Si/SiO<sub>2</sub> and Si/SiO<sub>x</sub>N<sub>y</sub> Interfaces**Jiro Ushio, Keiko Kushida-Abdelghafar<sup>1</sup>, and Takuya Maruizumi

Advanced Research Laboratory, Hitachi, Ltd.

1-280 Higashi-Koigakubo, Kokubunji-shi, Tokyo, 185-8601, Japan

Phone: +81-42-323-1111 (ext. 2706); Fax: +81-42-327-7804; E-mail: ushio@crl.hitachi.co.jp

<sup>1</sup>Central Research Laboratory, Hitachi, Ltd.

1-280 Higashi-Koigakubo, Kokubunji-shi, Tokyo, 185-8601, Japan

**1. Introduction**

In high-performance metal-oxide-semiconductor (MOS) devices, the thickness of the gate dielectric film is now 2 nm or less. In order to improve the electrical properties and reliability of such ultra-thin gate dielectric films, intensive studies are progressing. Nitrogen incorporation is one of the promising ways to modify a silicon dioxide film. However, it has been found to significantly increase degradation such as negative-bias temperature instability (NBTI) of a p-MOS device [1]. The NBTI of a silicon dioxide film has been known since the 1960's as a threshold voltage ( $V_{th}$ ) shift and a transconductance ( $G_m$ ) degradation caused by negative bias of the gate at high temperature. These stresses generate interface states and positive fixed charges in the Si/SiO<sub>2</sub> interface. It is commonly understood that the degradation mechanism involves hydrogen or water [1,2], but the role of nitrogen in the degradation is still unknown. For further understanding of NBTI, the atomistic structure around the nitrogen atom in the Si/SiO<sub>x</sub>N<sub>y</sub> interface must be revealed. Accordingly, to unveil the structure, x-ray photoelectron spectroscopy (XPS) measurements [3,4] and theoretical calculations [5] of the interface have recently been performed. As one of these studies, we investigated possible NBTI mechanisms and resultant structural changes at Si/SiO<sub>2</sub> and Si/SiO<sub>x</sub>N<sub>y</sub> interfaces. To determine if it is possible to identify a NBTI-generated structure through XPS of the interface, the N 1s core-level shifts of various structures at the Si/SiO<sub>x</sub>N<sub>y</sub> interface were also evaluated.

**2. Calculation**

The Si/SiO<sub>2</sub> and Si/SiO<sub>x</sub>N<sub>y</sub> interfaces trap holes during NBTI [2]. We hence investigated hole-trapping reactions at the interfaces by using model molecules for the interface structures. We assumed NBTI proceeds by either of two chemical reactions: a hydrogen-originated reaction or a water-originated one. By calculating the reaction energies for these reactions, we determined which reaction is dominant. We calculated the reaction energy by subtracting the total molecular energy before the hole-trapping reaction from that after the reaction. A smaller reaction energy corresponds to a more stable hole-trapped state; that is, such a reaction will occur more easily. Moreover, the activation energies for the reactions were calculated to know the kinetic aspects of the reactions. In the calculation of the N 1s core-level shifts of the nitrogen at the interface, we used model molecules that

can take account of the second-nearest-neighbor effect on the N atom [5]. We performed all the calculations by using the linear combination of Gaussian-type-orbitals density functional theory (LCGTO-DFT) program called deMon [6].

**3. Results***Chemical Reactions in NBTI*

Table I Reaction Energies of Hole-Trapping Reactions at Si/SiO<sub>2</sub> and SiO<sub>x</sub>N<sub>y</sub> Interfaces

Defect	Hole trapping reaction	Reaction energy
Water	$\text{H}_2\text{O} - \text{H} \xrightarrow{\text{h}^+} \text{H}^{\oplus} - \text{H}$	12.85 eV
Si-H bond	$\text{Si}-\text{H} \xrightarrow{\text{h}^+} \text{Si}^{\oplus} - \text{H}$	10.69 eV
At Si/SiO <sub>2</sub> interface		
No defect		9.99 eV
O vacancy		9.23 eV
At Si/SiO <sub>x</sub> N <sub>y</sub> interface		
No defect		7.89 eV
N vacancy		7.80 eV

The reaction energies for the hole-trapping reactions at the interface without hydrogen or water are listed in Table I and those with hydrogen or water are listed in Table II. From Table I, it is clear that the decrease in reaction energy corresponds to the order of H<sub>2</sub>O, SiH<sub>4</sub>, no defect at Si/SiO<sub>2</sub> interface, O vacancy at Si/SiO<sub>2</sub> interface, no defect at Si/SiO<sub>x</sub>N<sub>y</sub> interface, and N vacancy at Si/SiO<sub>x</sub>N<sub>y</sub> interface. We therefore consider that the hole-trapping sites are the O or N atom for the interface without a defect and the O or N vacancy for the interface with a defect. According to these two results, we assumed the schemes of the hydrogen- and water-originated reactions as in Table II, where the reactions begin with hole trappings at the sites described above followed by reactions with SiH<sub>4</sub> and H<sub>2</sub>O.

Each reaction in Table II is the one with the lowest reaction energy among all the reactions of each type. The hydrogen-originated reactions have a higher reaction energy than the water-originated reactions. That is, water is the

more important factor in causing NBTI. In the water-originated reactions,  $H_2O$  reacts with the O or N vacancy by inserting OH into the vacancy and generating a H atom to stabilize the hole-trapped state. In this way, the OH insertion increases the number of O atoms as the second-nearest neighbor of the N atom at the  $Si/SiO_xN_y$  interface. The water-originated reaction energy of the  $Si/SiO_xN_y$  interface is lower than that of the  $Si/SiO_2$  interface; thus, NBTI is enhanced by the N incorporation into the silicon dioxide film. Hence, we have to reduce water in the oxide film first to suppress NBTI. Note that the hydrogen-originated reaction is a cause of NBTI too, though its contribution is much less.

Table II Reaction Energies of Hydrogen- and Water-Originated Hole-Trapping Reactions at  $Si/SiO_2$  and  $SiO_xN_y$  Interfaces

Interface	Hole trapping	Reaction energy
Hydrogen-		
$Si/SiO_2$		9.19 eV
$Si/SiO_xN_y$		7.79 eV
Water-originated		
$Si/SiO_2$		7.83 eV
$Si/SiO_xN_y$		6.19 eV

#### N 1s Core-Level Shifts

The calculated N 1s core-level shifts shown in Fig. 1 agree well with those reported by Rignanese et al. [5]. We assumed that the main XPS peak of the N 1s core level in the  $Si/SiO_xN_y$  interface is due to structure (c) in Fig. 1 (as proposed by Kato et al.) [4]. The core level is considerably affected by the second-nearest neighbor atoms. Increasing the second-nearest-neighbor O atom shifts the N 1s core level

to higher energy by 0.3 to 0.8 eV. As described above, the water-originated NBTI reaction of the  $Si/SiO_xN_y$  interface increases the number of O atoms in the nearest neighbors of the N atom. Accordingly, the N 1s peak would become broader, but to observe this broadening the density of the hole-trapping sites must be large enough for XPS measurement.

#### 4. Summary

We investigated the chemical reactions causing negative-bias temperature instability (NBTI) of  $Si/SiO_2$  and  $Si/SiO_xN_y$  interfaces by using a first-principles molecular calculation, and of these reactions the water-originated reaction was found to be more important than the hydrogen-originated one. The increase of NBTI by N incorporation into the oxide film can be understood in terms of reaction energy. Moreover, the structural change caused by the NBTI can be identified by XPS measurement of the interface.

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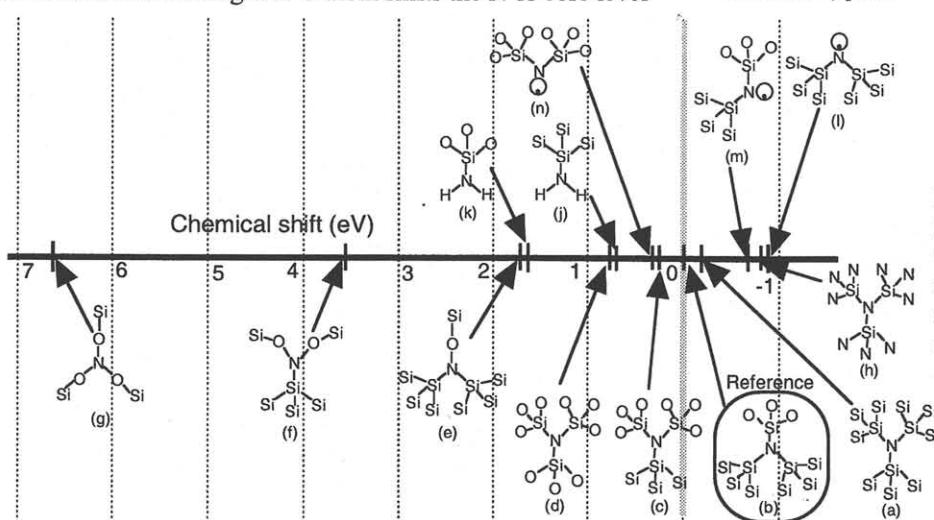


Fig. 1 Chemical shifts of N 1s core level for various structures (a-n) (including N in the  $Si/SiO_xN_y$  interface). For simplicity, the H atoms, which terminate the O and Si atoms, are not shown.