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Role of Hydrogen in Negative-Bias Temperature Instability

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1. Introduction

Reducing negative-bias temperature instability (NBTI) is an important issue in assuring reliability of complementary metal-oxide-semiconductor (CMOS) devices with an ultrathin gate dielectric. It is known that water and hydrogen are key species that cause NBTI.

In the present study, we focused on a hydrogen-originated reaction and investigated the specific role of hydrogen in it. Gerardi et al. [2] proposed that a hole-trapping Si-H bond releases a proton and forms a hydronium ion by bonding a water molecule to it. Jeppson and Svensson [3] showed another possible reaction, formation of a hydroxide group by reaction of a Si-H group and a Si-O-Si bond after trapping a hole at the oxygen atom. No valid reaction mechanism about hydrogen-originated NBTI is known yet, as is the case of water-originated NBTI.

Based on our preliminary investigation, it was assumed as the hydrogen-originated NBTI mechanism that the electrically neutral hydrogen atom of the Si-H bond possibly migrates to an oxygen or nitrogen atom or to an oxygen or nitrogen vacancy in the interface trapping a hole. Analysis of the hydrogen position in the Si/dielectric interface and the dielectric film is difficult to do experimentally. We, therefore, made full use of results obtained from first-principles calculations and investigated the energetics of hydrogen-originated NBTI reactions.

2. Calculation Details

We calculated hole-trapping energies of the hydrogen-originated reactions of the Si/SiO_2 and Si/SiO_xN_y interfaces with and without hydrogen migration by using model molecules for the interface structures (Fig. 1). We assumed that the structure of the Si/SiO_xN_y interface is that suggested by Takahashi et al.[4]. The model for N vacancy in the Si/SiO_xN_y interface is the same as that for O vacancy in the Si/SiO_2 interface. Si_4H_{10} was used as a model of the Si-H bond in the interfaces. The hole-trapping energy was obtained by subtracting the total energy of the model molecule before the hole-trapping reaction from that after the reaction. The total energies were calculated by fully optimizing the geometries of the model molecule for an electrically neutral state (before hole trapping) and a cationic state (after hole trapping). Accordingly, a plus sign of the hole-trapping energy implies that such a reaction is endothermic, i.e., thermodynamically hard to occur, and a minus sign shows that the reaction is exothermic, i.e., easy to occur.

It is known that more severe NBTI is observed at the Si/SiO_xN_y interface than at the Si/SiO_2 interface [2]. We investigated the cause of the difference between the Si/SiO_2 and Si/SiO_xN_y interfaces in relation to hydrogen-migration energy. We calculated the energies using molecules which model the interfaces (including Si-H bonds) in order to reproduce the migration of hydrogen adjacent to the site trapping a hole. The energy was calculated by subtracting the total energy of the model molecule in a cationic state before hydrogen migration from that after migration. By definition, as the hole-trapping energy, plus or minus signs of the energy infer that the migration is endothermic or exothermic. We performed all the calculations by using the linear combination of Gaussian-type-orbitals density functional theory (LCGTO-DFT) program called deMon [5].

3. Results

Hole-Trapping Reaction Energy

The hole-trapping reaction energies of the Si/SiO_2 and Si/SiO_xN_y interfaces with and without hydrogen migration are listed in Tables I and II. The result of the Si/SiO_2 interface shows that the no-defect interface, compared with the interface with an oxygen vacancy, has lower energy in the hole-trapping reaction with hydrogen migration. We see the similar result for the Si/SiO_xN_y interface (the energies of the nitrogen vacancy are the same as those of the oxygen vacancy in the Si/SiO_2 interface because of the same structure assumed). The hole-trapping reaction energies of the Si/SiO_2 interface are higher than those of the Si/SiO_xN_y interface. The interface is therefore more susceptible to NBT stress than the Si/SiO_2 interface.

The hydrogen migration destabilizes the no-defect Si/SiO_2 interface trapping a hole by about 0.4 eV (the migration is endothermic), while the no-defect Si/SiO_xN_y interface is stabilized by 0.1 eV (exothermic). This is another reason for more severe NBTI of the Si/SiO_xN_y interface.

Migration Energy of Hydrogen Adjacent to Hole-Trapping Oxygen or Nitrogen in the Interface

The hydrogen-migration energies of the hydrogen adjacent to the oxygen or nitrogen atom trapping a hole are shown in Fig. 2. The hole-trapping reaction energies of the interfaces with and without hydrogen migration are also shown. The migration of hydrogen from Si to an adjacent O trapping a hole needs extra energy of 0.45 eV, but that to adjacent N trapping a hole needs only 0.01 eV.

Consequently, the hydrogen migration in the Si/SiO_xN_y interface occurs much more easily than that in the Si/SiO_2 interface.

The hydrogen migration in both of the Si/SiO_2 and Si/SiO_xN_y interfaces changes the hole distribution significantly. The distribution is shown in Fig. 2, where the numbers near the atoms are the main components of the distribution. The sum of the quantities on all the atoms, though not shown here, is one. Without hydrogen migration, a hole mainly distributes on the Si atoms regarded as the Si substrate. Once a hydrogen atom migrates to an adjacent O or N atom, a hole localizes on the O or N atom. The hydrogen atom can thus be considered to play an essential role in generating a positive fixed charge in NBTI.

4. Summary

Using a density-functional method and molecular models of Si/SiO_2 and Si/SiO_xN_y interface structures, we investigated how hydrogen works in negative-bias temperature instability (NBTI). Reaction energies for hydrogen-originated hole-trapping reactions at the Si/SiO_2 and Si/Si_xN_y interfaces were evaluated. The hole-trapping reaction on the interfacial oxygen with hydrogen migration is endothermic, while that on the nitrogen is exothermic. Regardless of the hydrogen migration, the hole-trapping energy of the Si/SiO_xN_y interface is lower than that of the Si/SiO_2 interface. These results explain why NBTI is more severe at the Si/SiO_xN_y interface. It was also found that hydrogen localizes a hole on the oxygen or nitrogen bonded to the hydrogen; as a result, a positive fixed charge is generated in the interface.

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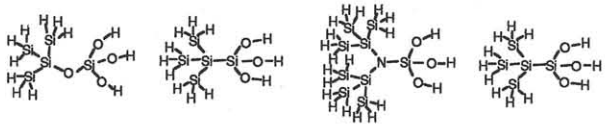


Fig. 1. Molecular models of Si/SiO_2 and Si/SiO_xN_y interfaces.

Table I. Hole-trapping reaction energies of Si/SiO_2 interface.

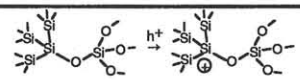
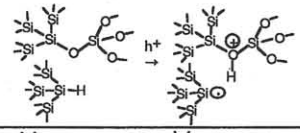
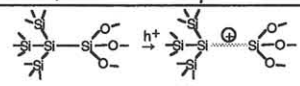
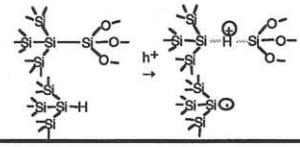
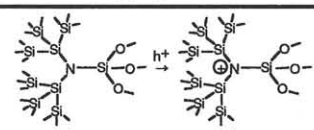
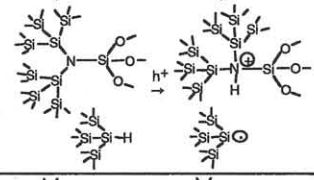
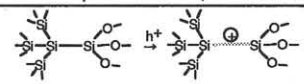
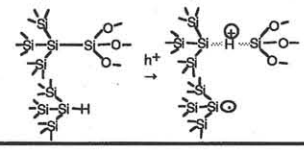
Interface structure	Hole trapping reaction	Reaction energy
No defect — Without H migration		8.14 eV
No defect — With H migration		8.53 eV
O vacancy — Without H migration		8.39 eV
O vacancy — With H migration		8.77 eV

Table II. Hole-trapping reaction energies of SiO_xN_y interface.

Interface structure	Hole trapping reaction	Reaction energy
No defect — Without H migration		7.52 eV
No defect — With H migration		7.42 eV
N vacancy — Without H migration		8.39 eV
N vacancy — With H migration		8.77 eV

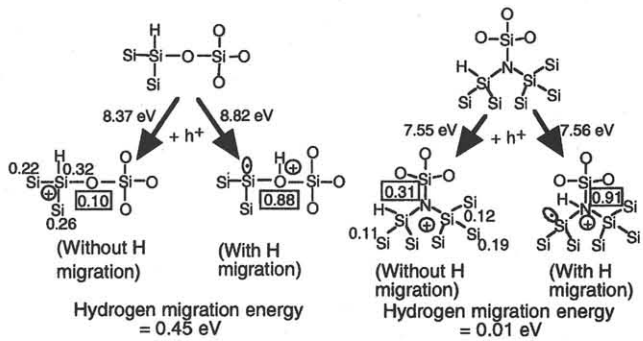


Fig. 2. Hydrogen-migration energies, hole-trapping reaction energies, and positive-charge distributions of hole trapped states of Si/SiO_2 and Si/SiO_xN_y interfaces.