Extended Abstracts of the 1998 International Conference on Solid State Devices and Materials, Hiroshima, 1998, pp. 488-489

Incorporation of N into Si/SiO_2 Interfaces: Molecular Orbital Calculations for Evaluating Interface Strain and Heat of Reaction

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1. Introduction

Nowadays, as metal-oxide-semiconductor (MOS) devices are scaled down, a more reliable gate insulator material than SiO_2 is needed. Silicon oxynitride is one alternative candidate that offers certain superior electrical properties to those of SiO_2. The cause of improvement by incorporating N into SiO_2, however, still remains unknown. Though it is observed that a significant amount of the incorporated N after oxynitridation of SiO_2 is mainly distributed close to the Si/SiO_2 interface [1], the relation between the electrical properties and the concentration profile of the incorporated N is not known. Lu et al. attributed the concentration profile to a reduction in the mismatch-induced strain with the inclusion of N near the interface [2], while Carr et al. explained the N distribution in terms of a reaction involving atomic oxygen that removes previously incorporated N from the oxide during a rapid thermal oxidation process in N_2O [1]. In the present study based on molecular orbital calculations, we investigate the incorporation of N into the Si/SiO_2 interfaces from two viewpoints: the change in the strain energy of the $Si(100)/SiO_2$ interfaces caused by N incorporation; and the heat of reaction for N incorporation into the Si/SiO_2 interfaces. From the obtained results, we will find the driving force for the N accumulation at the interface.

2. Calculation Details

We devised a method to calculate the strain energy at the Si/SiO_2 interface by using molecular models. First, we fully optimized the structure of a $Si\text{-}SiO_2$ cluster, which is a model of the Si/SiO_2 interface. Next, we obtained each of the Si and SiO_2 clusters by separating the Si and SiO_2 parts of the $Si\text{-}SiO_2$ cluster. The dangling bonds newly generated by the separation were terminated by H atoms. We then optimized the positions of only these H atoms of each cluster while fixing the positions of all other atoms of the cluster. We considered the obtained total energies of the Si and SiO_2 clusters as the energies of the Si and SiO_2 clusters forced to form the Si/SiO_2 interface. We call these total energies the constrained-state energies of the Si and SiO_2 clusters. Furthermore, we fully optimized the whole structures of the Si and SiO_2 clusters and refer to the resultant total energies as the free-state energies of the Si and SiO_2 clusters. The energy difference between the constrained and free states of a Si or SiO_2 cluster corresponds to the strain energy of a Si or SiO_2 cluster. In the same way, we can also evaluate the strain energies of the Si and SiO_2 clusters with N. The difference between the strain energies of the Si/SiO_2 interfaces with and without N is defined as the strain-energy change caused by N incorporation.

Observations by transmission electron microscopy and x-ray scattering showed that the two SiO_2 structures (a cristobalite-like one and a tridymite-like one) can be assumed as the structures of the SiO_2 film. With each SiO_2 structure, we investigated four types of N incorporation into the Si/SiO_2 interface (Fig. 1). All these types include the $N{\equiv}Si_3$ (silicon-nitride) bonds, which are thought to play a dominant role in strain reduction at the interface [2].

We also investigated, only for the cristobalite-like SiO_2, the effect of different types of oxygen-vacancy interfacial defects on the strain energy change by N incorporation. The schematic structures of the defects are shown in Fig. 2 and are denoted as the (+1/+3), (+1/+2), and (0/+3) defects referring to the oxidation numbers of the Si atoms around the defects. We assumed the N incorporation occurs at the defect site where the $N{\equiv}Si_3$ bonds are formed.

Heats of reaction for the N incorporation reactions using NO and N_2O gases in the Si and SiO_2 films were calculated by using the following model reactions (where the stoichiometric coefficients are neglected for simplicity).

$$H_3Si\text{-}SiH_3 + (NO \text{ or } N_2O) \rightarrow N{\equiv}(SiH_3)_3 + H_3Si\text{-}O\text{-}SiH_3 \quad (1)$$

$$(HO)_3Si\text{-}O\text{-}Si(OH)_3 + (NO \text{ or } N_2O) \rightarrow N{\equiv}(Si(OH)_3)_3 + O_2 \quad (2)$$

All calculations were performed using the AM1 method with MOPAC Ver. 6.02 [3].

3. Results

The $Si\text{-}SiO_2$ clusters used in the calculations consist of about 60 to 160 atoms. The obtained strain-energy changes are listed in Table I. A positive value for the energy change means the strain energy of the cluster has increased. In all the cases the strain energies of the Si clusters increase. The strain energies of the SiO_2 clusters decrease for some cases. The amount of decrease for the interface without defects is much smaller than that of the increase for the Si clusters, though the amount of decrease for the SiO_2 cluster with the oxygen vacancy defect (+1/+3) or (+1/+2) is significantly large, -0.55 eV or -0.38 eV, respectively. As a result, in total, the N incorporation increases the strain energy of the Si/SiO_2 interface without defects, but it decreases the strain energy for some Si/SiO_2 interfaces with the defect.

The heats of reaction for reactions 1 and 2 are listed in Table II. Reaction 1 is exothermic, while reaction 2 is endothermic. This means the incorporation reaction cannot occur in the SiO_2 film but can occur in the Si film. Consequently, NO or N_2O gas goes through the SiO_2 film

without any reaction and reacts with the Si film at the interface. This simply explains the concentration profile of the N incorporated into the Si/SiO_2 interface.

The heat of reaction in the Si film is large enough to overcome the increase of strain generated by the reaction of the Si/SiO_2 interface without defects and is even much larger than the amount of strain energy decrease of the interface with the defect. The heat of reaction for N incoporation reaction must be the dominant factor for the N accumulation at the interface.

4. Conclusions

Using molecular orbital calculations, we evaluated the strain energies at Si/SiO_2 interfaces (with and without N incorporation) and the heats of reaction for the N incorporation reactions. The amount of strain energy reduction is much smaller than the heat of reaction for the N incorporation in the Si film. Therefore, the remarkable difference between the heats of reaction for the N incorporations in Si and SiO_2 is the primary driving force for the N accumulation at the interface.

Acknowledgments

We thank Mr. Nobuyoshi Natsuaki, Mr. Makoto Ogasawara, Mr. Satoshi Sakai and Dr. Hisako Satoh of the Devices Development Center, Hitachi, Ltd. for their stimulating discussions.

References

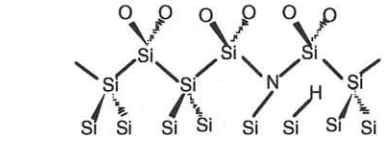
1) E. C. Carr, K. A. Ellis, and R. A. Burrman, Appl. Phys. Lett., **66**, 1492 (1995).
2) Z. H. Lu, S. P. Tay, R. Cao, and P. Pianetta, Appl. Phys. Lett., **67**, 2836 (1995).
3) MOPAC Ver.6, J. J. P. Stewart, QCPE Bull., **9**, 10 (1989); Revised as Ver. 6.01 by Tsuneo Hirano, University of Tokyo, for HITAC and UNIX machines, JCPE Newsletter, **1**, 10 (1989); Revised as Ver. 6.02 by the present authors.

Table I Strain energy changes (eV) caused by incorporation of N into the Si/SiO_2 interfaces.

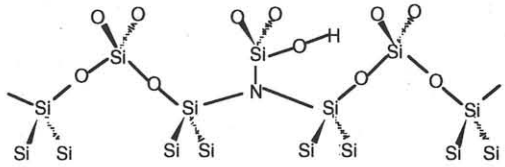
Type of N incorporation	Cristobalite-like SiO_2			Tridymite-like SiO_2		
	Si film	SiO_2 film	total	Si film	SiO_2 film	total
Substitution of Si	1.67	-0.25	1.42	0.08	-0.02	0.06
Substitution of O	1.17	0.25	1.42	1.08	-0.04	1.04
Addition into Si film	0.48	0.03	0.51	0.24	-0.03	0.21
Addition into SiO_2 film	—	—	—	1.36	0.29	1.65
Addition into (+1/+3) defect	0.09	-0.64	-0.55	—	—	—
Addition into (+1/+2) defect	0.29	-0.67	-0.38	—	—	—
Addition into (0/+3) defect	0.83	-0.02	0.81	—	—	—

Table II Heats of reaction (eV) for the incorporation reaction of N into the Si/SiO_2 interface.

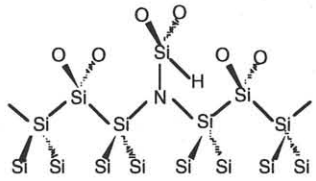
Reaction	NO gas	N_2O gas
1	6.01	10.50
2	-4.95	-7.18



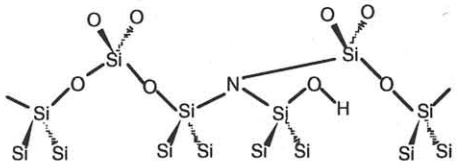
(a) Substitution of Si with N



(b) Substitution of O with N

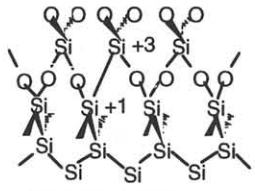


(c) Addition of N into Si film

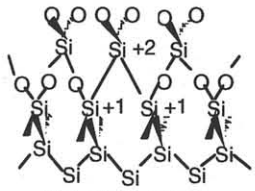


(d) Addition of N into SiO_2 film
(only for tridymite-like SiO_2)

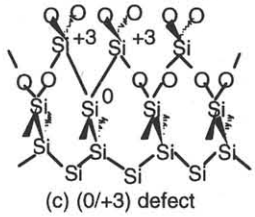
Fig. 1 Four types of N incorporation into the $Si(100)/SiO_2$ interface.



(a) (+1/+3) defect



(b) (+1/+2) defect



(c) (0/+3) defect

Fig. 2 Three types of oxygen-vacancy defect at the Si(100)/cristobalite-like SiO_2 interface.