# *Ab initio* Study of Boron Pile-up at the Si(001)/ SiO<sub>2</sub> Interface

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Abstract—We studied the atomistic structure of boron atom at the Si(001)/SiO<sub>2</sub> interface using ab initio calculation method to investigate the mechanism of boron pile-up at the interface. We found that, if there is no defects, such as oxygen vacancy, at the interface, no stable sites of B would appear at Si/SiO<sub>2</sub> interface and SiO<sub>2</sub> layer, thus indicating that boron in silicon will only diffuse to the interface, but not segregate across the interface, unless additional defects or impurities exist. By introducing oxygen vacancy and H bonds, we found some stable configurations at Si/SiO<sub>2</sub> interface, which can support the mechanism of boron segregation at Si(001)/SiO<sub>2</sub> interface. Therefore, we assume that vacancy of O and H bonds may play a crucial role in segregation by opening additional trapping sites. Furthermore, we also found the largest energy difference between B at Si/SiO2 interface and that in deep bulk Si is about 2.9eV, which is in agreement with experimental boron activation energy of emission from Si/SiO<sub>2</sub> value of 2.64eV.

#### Keywords- Si/SiO<sub>2</sub> interface; pile-up; ab initio; boron

# I. INTRODUCTION

The continued scaling of Si MOSFETs to deep submicron dimensions requires ultrashallow  $p^+/n$  junctions to suppress the short-channel effect. Interface effects have been increasingly important for determination of dopant profiles. One of such important effects is dopant segregation at the Si/SiO<sub>2</sub> interface. In MOSFETs, segregation to Si(001)/SiO<sub>2</sub> interfaces can cause redistribution of dopants during the process of fabrication. This effect is especially significant in "decanano" devices and can affect the MOSFET threshold voltage by up to 50%[1]. Recently, some experimental and theoretical works on this subject have been conducted. Ghetti et al. [2] studied the boron channel profile's dependency on width of active area due to lateral segregation. Shima et al. [3] found that the pile-up of boron is mainly on the interface and within 0.6nm of the Si side. The likelihood of boron pile-up in the interstitial state was also studied. According to their studies, activation energy for boron emission from the Si(001)/SiO<sub>2</sub> interface to bulk silicon using BF<sub>2</sub> implant is 1.68eV. However, a more recent experiment by Tsuji et al.[4] provided a different activation energy of 2.64eV, indicating that the lower activation energy given by Shima et al. could be affected by the presence of fluorine, for nuclear reaction analysis (NRA) measurements found that F as well as B are trapped at the  $Si(001)/SiO_2$  interface after annealing in nitrogen ambient. Dabrowski et al. [5] presented a model of donor segregation based on a combined trapping/paring model, using phosphorus as a typical example of a donor and guided by results of ab initio calculations. Ravichandran et al. [6] studied the influence of hydrogen and point defects on arsenic segregation at Si(001)/SiO<sub>2</sub> interface using *ab initio* calculations, indicating the inclusion of hydrogen into the modeling may help explain the difference between the previous model [5] and the experiments. Furuhashi et al. [7] studied atomic configuration of boron pile-up at the Si(001)/SiO<sub>2</sub> interface using *ab initio* calculations. They chose tridymite SiO<sub>2</sub> structure of a thin oxide layer of the interface model. They only investigated substitutional B replaced by a Si atom, with and without existence of an O vacancy. They found B atom is stable in oxide layer of the interface which includes an oxygen vacancy as a point defect and one H termination. The total energy of B at interface is 1.2eV lower than that in deep bulk Si. Although the value is still much smaller than experimental result of 2.64eV, their calculation revealed that the defects at  $Si/SiO_2$ interface may play an important factor in clarifying the mechanism of B pile-up.

Based on previous experimental and theoretical studies and in pursue of a better understanding of the physical mechanism of boron pile-up at the  $SiO_2/Si(001)$  interface, we investigated more extensive boron atomic configurations at  $SiO_2/Si(001)$ interface using *ab initio* study method.

#### II. CALCULATION DETAILS

The interface structure we examined was proposed by Kaneta *et al.* [8], in which the periodic structure contains a Si substrate of 7ML, an about 10 Å thick layer for quartz SiO<sub>2</sub>, and a 10 Å vacuum region including 175 atoms. The interface unit cell is Si(001)-( $2\times2$ )(a=5.38 Å). Figure 1. displays the basic supercell as the perfect Si(001)/SiO<sub>2</sub> interface used in the study. The dangling bonds in the Si and SiO<sub>2</sub> surface are terminated with H atoms. All the calculations are performed in neutral state.

We adopted the CASTEP [9] density functional electronic structure package and the PBE [10] generalized gradient approximation (GGA) for the exchange-correlation function (which has been proven to be effective and capable of generating very accurate structures in many previous defect studies) with a plane-wave basis set in our calculation. We used a Vanderbilt ultra-soft pesudopotential [11] for Si, B, O and H. Numerical convergence was verified by performing test calculations at plane-wave cut-off between 260eV and 330eV and with Brillouin zone sampling [12] to  $\Gamma$  and  $2 \times 2 \times 2$ of  $2 \times 2$  surface cells. The data quoted below were obtained using cutoff of 260eV and  $\Gamma$  point. The estimated numerical uncertainty in energy differences is about 0.3eV, which is due to Brillouin zone sampling and the energy cutoff. In order to minimize the electronic energy, a density mixing scheme was utilized [13], whereas for minimization of ionic energy, Hellmann-Feynman theorem was utilized to calculate forces and also as a conjugate gradient scheme [14]. The relaxation of all configurations used in these calculations proceeds till the Hellmann-Feynman force is not greater than 0.03 eV/Å, which was found to converge atomic positions to better than 0.01 Å.



Figure 1. The  $Si/SiO_2$  interface structure used in our calculation, where Si, O and H atoms are drawn in yellow(white), red(black) and cyan(small white) respectively.

#### III. RESULTS AND DISCUSSION

In order to examine the relevancy of potential further trapping mechanism, we investigated various B-related structures at  $Si/SiO_2$  interface. We moved these structures to positions at various distances away from the  $Si-SiO_2$  interface to observe the energies at each location and locate positions where they are the most stable. By comparing energies of these structures in bulk Si, at  $Si/SiO_2$  interface and inside  $SiO_2$  layer, the most stable positions, which could be responsible for trapping of B atoms, can be found. We categorized the structures in our calculations into two classes: One is  $Si/SiO_2$  interface with defects. Our calculation suggests defects have an important role in B pile-up at  $Si/SiO_2$  interface by opening additional trapping sites. The results are tabulated in Table I.

#### A. Si/SiO<sub>2</sub> interface without defects

At a first step calculation, we examined Bs(Si), a Si atom in lattice position replaced by a B atom. The relative energy as a function of B sites near the perfect Si/SiO<sub>2</sub> interface is shown in Figure 2. The total energy in SiO<sub>2</sub> layer increases steeply up to 2.03eV higher than that when B is in deep bulk Si site, indicating Bs(Si) configuration may not be responsible for trapping B atom at the Si/SiO<sub>2</sub> interface. The result is in agreement with Furuhashi *et al.*'s value of 2.2eV [7]. It is obvious in Figure 2. that no major energy difference occurs when B approaches interface from in deep bulk Si, thus suggesting that B atoms could move to the interface but will not have segregation.



Figure 2. Bs energy at different position in the vicinity of Si/SiO2 interface.

Ravichandran *et al.* [6] calculated total energy of a substitutional As atom in the different position near  $Si/SiO_2$  interface. The total energy increases steeply up to about 8eV when the As atom is moved from bulk Si to  $SiO_2$  layer, revealing similar tendency with B.

Although no stable substitutional site for B exists near Si/SiO<sub>2</sub> interface, we still can not assert that Bi (interstitial B) is unable to diffuse to SiO<sub>2</sub> layer for the possiblity that some stable configurations for Bi in SiO<sub>2</sub> layer or near interface still remains. Then we calculated configurations of a Bi locating in different sites near Si/SiO2 interface. To our knowledge, such calculation were never conducted before. When Bi is in bulk Si, the most stable Bi is Bs-I(T), a B atom at substitutional site and a Si interstitial at a neighboring tetrahedral position. When Bi is in  $SiO_2$  side, we chose some configurations proposed by Otani et al.[15] who studied B diffusion in quartz-SiO<sub>2</sub>. We searched for stable configurations near interface that is different from the most stable configuration in bulk Si and SiO<sub>2</sub> layer. Figure 3. shows two stable configurations near Si/SiO<sub>2</sub> interface. We found out that the energy of the most stable Bi in bulk Si is about 0.5~1eV lower than Bi at Si/SiO<sub>2</sub> interface, and about 2eV lower than that in SiO<sub>2</sub> layer. These results suggest that Bi could not diffuse into SiO2 layer from bulk Si.



Figure 3. View down the <100> direction of some stable Bi configurations in (a) bulk Si (b) Si/SiO<sub>2</sub> interface. The Si, B, O atoms are drawn in yellow(light grey), grey(big) and red(black) respectively.

Combined with the results of subsitutional B, it is found that, for the perfect  $Si/SiO_2$  interface, the most stable sites of B is in bulk Si. It is possible for B to diffuse to the interface,

but there will not be segregation, contrary to the experimental observations.

# B. $Si/SiO_2$ interface with an O vacancy and H terminations

During fabrication of  $Si/SiO_2$  interface, there appeared a large amount of point defects in  $SiO_2$  layer, such as O and Si vacancies with dangling bonds since thermal  $SiO_2$  is grown into amorphous phase. Furthermore, additional experimental data seem to indicate significant presence of hydrogen even in nominally pure oxides, resulting in significant enhancement of diffusion. Hydrogen is usually introduced to passivate dangling bonds in the oxide and at the interface [16]. Based on these experimental evidences, it is necessary to examine B-related structures in the presence of defects. Therefore, by introduction of O vacancy as well as H into account, four kinds of structures are considered:

1) Bi-V(O) (an interstitial B atom and an O vacancy);

2) Bs(Si)-H (a Si atom replaced by a B atom and an H atom);
3) Bs(Si)-V(O)-H (a Si atom replaced by a B atom, an O vacancy and an H atom);

4) Bi-V(O)-H (an interstitial B, an O vacancy and an H atom).

The first structure does not involve H terminations. H terminations are used to passivate dangling bonds in the last three configurations.

# 1) Bi-V(O)

In this structure, an O vacancy is introduced into the perfect interface. It should be noticed that O vacancy locates only in SiO<sub>2</sub> layer. The B atom will exhibit different forms when locating in Si and SiO<sub>2</sub> side. When the B atom is in Si side, it is an interstitial B atom and Bs-I(T) is considered as the most stable structure. When in SiO2 side, it will occupy O vacancy to form a substitutional B but at O lattice site. When the B atom is at the Si/SiO<sub>2</sub> interface, the total energy is 1.3eV lower than in bulk Si. The configuration is shown in Figure 4. And when B is in SiO<sub>2</sub> side, the total energy increases greatly to 0.24eV higher than that in bulk Si. The results suggest that a B atom may be trapped in an O vacancy at the interface, but it could not stay stable in the O vacancy site in SiO<sub>2</sub>. The energy difference of 1.3eV is smaller than experimental value, i.e., 2.64eV[4].

#### 2) Bs(Si)-H

In the structure, a Si atom is replaced by a B atom. For a group-V atom, it is more convenient to occupy a threefold-coordinated site on the surface of a group-IV semiconductor, where it can be electrically neutral, than to substitute a fourfold-coordinated in bulk crystal. Here, an H atom is used to terminate a dangling bond. The results are as shown in Table I. It is found that the energy difference is very small comparing B in bulk Si and at the Si/SiO<sub>2</sub> interface, and the energy increases rapidly when B is moved into bulk SiO<sub>2</sub>. The tendency is quite similar with structure Bs(Si).



Figure 4. View down the <100> direction of the most stable Bi-V(O) configurations The Si, B, O atoms are drawn in yellow(light grey), grey(big) and red(black) respectively.

# 3) Bs(Si)-V(O)-H

The structure is originated from Bs(Si)-V(O), in which the B atom occupies a substitutional position of a lattice Si and a H atom is used to terminate a dangling bond introduced by O vacancy. Furuhashi *et al.* [7] studied a similar structure of Si and tridymite phase SiO<sub>2</sub> interface. They used 0, 1 and 2 H terminations in an O vacancy respectively. Figure 5. shows two configurations of Bs(Si)-V(O)-H structure.



Figure 5. View down the <100> direction of Bs(Si)-V(O)-H configurations in (a) bulk Si (b) Si/SiO<sub>2</sub> interface. The Si, B, O, H atoms are drawn in yellow(light grey), grey(big), red(black) and white(small) respectively.

It is found that B at  $Si/SiO_2$  is the most stable configuration of Bs(Si)-V(O)-H structure, as shown in Figure 5(a). The energy is 0.35eV lower than B in bulk Si. Furuhashi *et al.* also found B is the most stable at the interface when one H termination is in an O vacancy, but the energy difference is 1.2eV, much larger than ours. The difference may mainly come from different SiO<sub>2</sub> structures. Our calculation suggests the same tendency as Furuhashi *et al.* 's result. They also found that, B is the most stable in bulk Si when no H termination exists and two H terminations are in an O vacancy.

# 4) Bi-V(O)-H

This structure is originated from Bi-V(O). An H atom is used to terminate a dangling bond introduced by O vacancy or B atom. The O vacancy only locates in SiO<sub>2</sub> layer and the B atoms exhibit different forms when in bulk Si and in SiO<sub>2</sub> side respectively. When the B atom is at Si side, it is an interstitial B atom and Bs-I(T) configuration is considered as the most stable. One H atom is used to terminate a dangling bond of an O vacancy. When B is at SiO2 side, it will occupy O vacancy to form a substitutional B but at O lattice site. The H atom is used to terminate a dangling bond of B.



Figure 6. View down the <100> direction of Bi-V(O)-H configurations in (a) bulk Si (b) Si/SiO<sub>2</sub> interface and (c) SiO<sub>2</sub> layer. The Si, B, O, H atoms are drawn in yellow(light grey), grey(big), red(black) and white(small) respectively.

Figure 6. shows three configurations of Bi-V(O)-H. in which B lies in bulk Si side, Si/SiO<sub>2</sub> interface and SiO<sub>2</sub> side respectively. Our calculations indicates that B is the most stable when at Si/SiO<sub>2</sub> interface, 2.9eV lower than B in bulk Si, suggesting an O vacancy with an H termination may trap interstitial B to form a very stable configuration. It also can be found that the energy of B in SiO<sub>2</sub> is 2.0eV lower than that in bulk Si, but about 0.9eV higher than B at Si/SiO2 interface. The results suggest that the interface functions as a sink to trap interstitial B in bulk Si. The reason that B becomes stable at the interface could be that an H atom and two bridge O atoms form a stable threefold coordinated site for B atom. Without H termination, namely in structure Bi-V(O), the energy of B at interface is also lower than that in bulk Si, but the value is about 1.5eV higher than that with H termination. It is also worthy note that, with H termination, the energy of B in SiO<sub>2</sub> layer is much lower than that in bulk Si but higher in Bi-V(O) structure. We assume that H plays a crucial role in segregation by opening additional trapping sites for B. Similarly, the presence of H has been suggested to influence B segregation upon annealing[17], where a similarly high binding energy between B and H is found in calculations. Tsuji et al. [4] measured boron's emission rate from Si/SiO<sub>2</sub> interface traps to bulk Si. They gave an activation energy of 2.64eV which is in agreement with the value of 2.9eV in our calculation for Bi-V(O)-H structure.

# IV. CONCLUSION

We made extensive investigation of B atomistic structure at  $Si(001)/SiO_2$  interface. Our calculations strongly suggest that, without the inclusion of defects (such as O) and H, there would be no stable sites of B at  $Si/SiO_2$  interface and  $SiO_2$ layer. And also, the energy of B in  $SiO_2$  layer is much higher than that in bulk Si. The results mean that B in Si will only diffuse to the interface, but will not segregate across the interface. After introduction of O vacancy and H, we found, in Bi-V(O), Bs(Si)-V(O)-H and Bi-V(O)-H structures, a B atom may become stable at Si/SiO<sub>2</sub> interface. In Bi-V(O)-H structure, the B atom forms threefold coordination structure at Si/SiO<sub>2</sub> interface and in SiO<sub>2</sub> layer. The energy difference between B at Si/SiO<sub>2</sub> interface and in bulk Si is quite high, namely 2.9eV, which is in agreement with experimental result of 2.64eV. Thus we assume that H and vacancy of O may have a crucial role in segregation by opening additional trapping sites. Our calculation shows that the segregation driving force is dramatically enhanced in the presence of H, which is usually introduced to passivate dangling bonds in the oxide and at the interface. We hope our calculation can provide some microscopic physical insight to the mechanism of B pile-up at Si/SiO<sub>2</sub> interface and help improve the corresponding continuum models.

Table I. Relative energies of various B configurations at  $\mathrm{Si}/\mathrm{SiO}_2$  interface

	Bulk Si (eV)	$Si/SiO_2(eV)$	SiO <sub>2</sub> layer (eV)
Bs(Si)	0	1.20	2.03
Bi	0	0.5~1.0	~2.0
Bi-V(O)	0	-1.30	0.24
Bs(Si)-H	0	-0.05	1.66
Bs(Si)-V(O)-H	0	-0.35	0.24
Bi-V(O)-H	0	-2.9	-2.1

#### REFERENCES

- H. -H. Vuong, C. S. Rafferty, S. A. Eshraghi, J. L. Lentz, P. M. Zeitzoff, M. R. Pinto, and S. J. Hillenius, IEEE Trans. Electron Devices 43, 1144 (1996).
- [2] A. Ghetti, A. Benvenuti, G. Molteni, S. Alberici, V. Soncini and A. Pavan, IEDM 2004.
- [3] A. Shima, T. Jinbo, N. Natsuaki, J. Ushio, J. H. Oh, K. Ono and M. Oshima, J. Appl. Phys. 89, 3458 (2001).
- [4] H. Tsuji, M. Furuhashi, M. Tachi and K. Taniguchi, Jpn. Appl. Phys. 44, 143 (2005).
- [5] J. Dabrowski, H.-J. Müssig, V. Zavodinsky, R. Baierle, and M. J. Caldas, Phys. Rev. B. 65, 245305 (2002).
- [6] K. Ravichandran and W. Windl, Appl. Phys. Lett. 86, 152106 (2005).
- [7] M. Furuhashi, T. Hirose, H. Tsuji, M. Tachi, and K. Taniguchi, IEICE Electronics Express, 1, 126(2004).
- [8] C. Kaneta and T. Yamasaki, Micro. Eng. 48, 117(1999).
- [9] CASTEP, MS Modeling Getting Started, San Diego: Accelrys Software Inc., 2004.
- [10] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865(1996).
- [11] D. Vanderbilt, Phys. Rev. B 41, 7892(1990)
- [12] H. J. Monkhorst and J. D. Pack Phys. Rev. B 13, 5188(1976).
- [13] G. Kresse and J. Furthmuller Phys. Rev. B 54 11169(1996)
- [14] M. Scheffler, J. P. Vigneron and G. B. Bachlet, Phys. Rev. B 31 6541(1985)
- [15] M. Otani, K. Shiraishi, and A. Oshiyama, Phys. Rev. Lett. 21, 075901(2003).
- [16] P. Balk, Microelectron. Eng. 48, 3(1998).
- [17] K. A. Ellis and R. A. Buhrman, Appl. Phys. Lett. 74, 967(1999).