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Tight-Binding Quantum Chemical Molecular Dynamics Simulations on Low Energy Boron Implantation Process into Silicon Surface

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The creation of shallow junctions in the semiconductor industry is a crucial step for the development of future electronic device and requires low energy boron implantation process. In the present study, we have statistically investigated the dynamic behavior of boron implantation process into silicon surface by using our original tight-binding quantum chemical molecular dynamics method, which is more than 5000 times faster than conventional first-principles molecular dynamics method. Boron atom was found to have a tendency to diffuse along <110> direction in silicon crystalline and to occupy interstitial hexagonal site, dominantly. The statistical analyses indicate that the reflection ratio and depth profile of the implanted boron atom strongly depend on the initial kinetic energy and incident direction.

Key words: Ultra-shallow Junction, Boron Implantation, Tight-Binding Quantum Chemical Molecular Dynamics, Silicon Semiconductor

1. INTRODUCTION

Diminishment of the microelectronic devices in the modern integrated circuits requires fabrication of ultra-shallow junctions for silicon CMOS devices. In order to realize boron doped layers shallower than 50 nm, the implantation of boron at ultra low energies in crystalline silicon (< 1 keV) is the major candidate. However, this process has some problems due to transient enhanced diffusion of boron and the particular difficulty in construction of very shallow boron doped layers. Therefore, detailed understanding of the phenomena at the surface during the low energy boron implantation process can facilitate the development of this technique.

In order to analyze the semiconductor processes, computer simulation has been very effective tool. Among a lot of simulation methods, classical molecular dynamics calculations have been used to study the dynamic behavior of various processes at the surface. However, it is difficult to apply these methods to unknown systems because empirical interatomic potentials are employed in the methods. Furthermore, these calculations provide no information about electronic properties and hence chemical reaction dynamics is not accurately simulated [1,2]. On the other hand, first-principles calculations have provided accurate descriptions of the electronic states of the system and have been applied to various systems such as impurity state in silicon [3-6] and so on. However these calculations request huge computational costs and the applications have been limited to very small systems. Therefore, it is unrealistic to simulate the ion implantation process, which requires a large simulation model by the first-principles calculation.

Hence, we have recently succeeded in the development of a tight-binding quantum chemical molecular dynamics program, based on our original tight-binding approximation [7-11]. This program is over 5000 times faster than the conventional first-principles molecular dynamics approach. This program enables us to simulate the chemical reaction dynamics considering the electronic states on large simulation model. Hence in the present study, we applied the above new simulation software to the investigation of boron implantation processes into silicon surface.

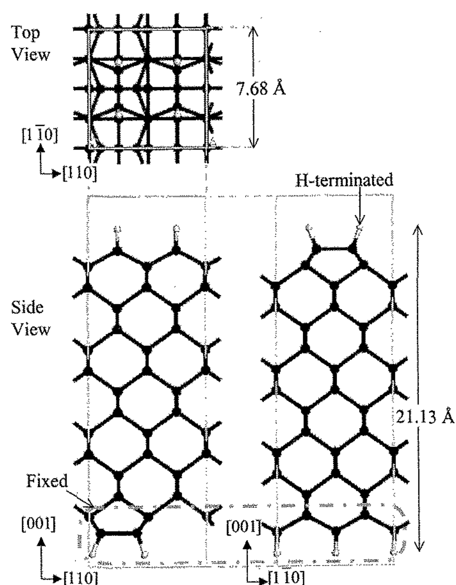

Fig. 1 H-terminated Si(001) 2×1 surface model

2. METHOD

Our tight-binding quantum chemical molecular dynamics program "Colors" based on our original tight-binding approximation is employed to simulate boron implantation into silicon surface. This program employs some parameters in order to accelerate the quantum chemical molecular dynamics calculations. If these parameters are determined as to fit the experimental results empirically, it is impossible to apply this program to unknown system. Therefore, we developed a new methodology to determine all the parameters as to fit the first-principles calculation results. This methodology enables us to perform fast and accurate quantum chemical molecular dynamics simulations. The detailed descriptions are reported elsewhere [7-11].

After the parameterization, we performed quantum chemical molecular dynamics simulation for the low energy boron implantation process into the silicon surface. Dimer reconstructed Si (001) 2×1 surface was used as a substrate and their dangling bonds were terminated by hydrogen atoms (Fig. 1). The substrate consisting of 68 atoms with a surface area of 58.98 Å^2 (7.68 Å × 7.68 Å) was used for the present simulations.

First, in order to investigate the stability of the substituted boron atom in the silicon surface, the geometry optimizations of various boron-doped silicon surface models were carried out. Second, quantum chemical molecular dynamics simulations on the implantation process of boron atoms into silicon surface were performed. In the above simulations, boron atoms were bombarded onto the silicon substrate with initial kinetic energies of 50, 100, and 200 eV. The incident boron atom was placed at 7.9 Å above the surface with a random (x, y) position. 50 different (x, y) initial positions of boron atom were chosen and the results were statistically analyzed. All the simulations were performed at 300 K with a time step of 0.1×10^{-15} s.

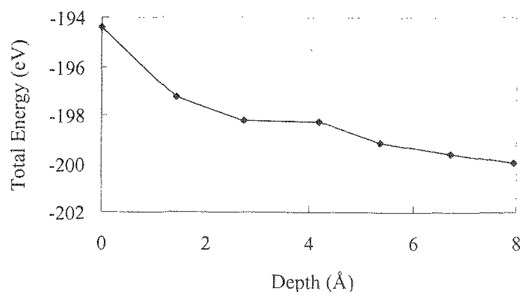

Fig.2 Total energy of boron-doped H-terminated Si (001)2×1 surface depending on the depth of substituted boron atom.

3. RESULTS AND DISCUSSION

First, the effect of substitution site of boron atom on the stability of the system was investigated by the static tight-binding quantum chemical calculations. Fig. 2 shows the total energies of the boron-doped H-terminated Si (001) 2×1 surface depending on the depth of the substituted boron atom. This figure indicates that the substitution of boron atom in the deeper layer leads to the lower total energy of the system. Distributions of atomic charge and orbital were also analyzed for each substituted structure. Charge distributions of the boron-doped H-terminated silicon surface, in which one silicon atom at the depth of 7.96 Å was replaced by the boron atom, were shown in Fig. 3(a). In this figure, positively charged atoms are denoted by darker color while negatively charged atoms are represented by lighter color. This figure indicate that boron atom is negatively charged and silicon atoms connecting to the boron atom are also a little negatively charged. Two of the silicon atoms connecting to boron atom at deeper layer have less negative charge (q = –0.004) than other two silicon atoms at the shallower layer (q = –0.037). In all the other models, similar tendency was observed. The other silicon atoms are a little positively charged (q = 0.005~0.02). Fig. 3(b) shows the distribution of the acceptor level. The acceptor level is localized at only deeper layer around the boron atom.

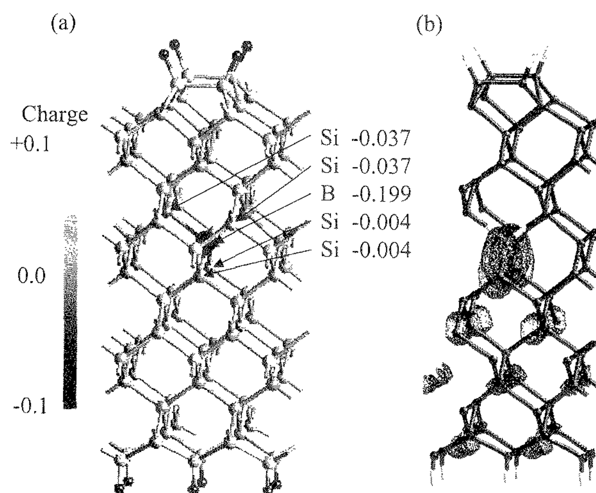

Fig.3 (a) Charge distribution and (b) acceptor level of boron-doped H-terminated Si(001)2×1 surface, in which one silicon atom at the depth of 7.96 Å was replaced by boron atom.

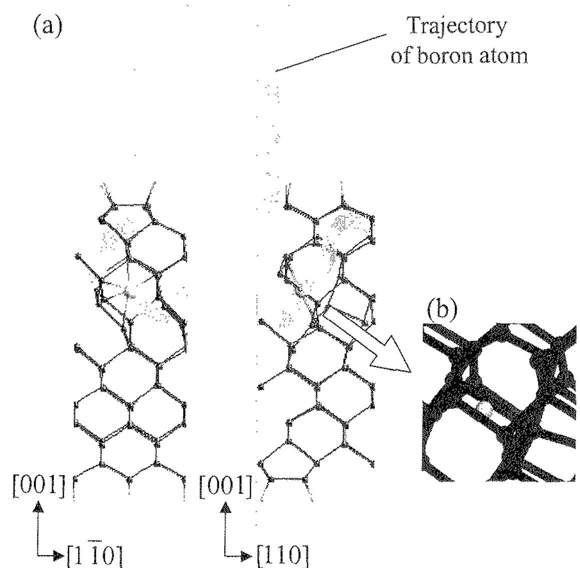

Fig.4 (a) Lateral views of boron implantation process when it was bombarded with initial kinetic energy of 50 eV (larger circle indicates boron atom) and (b) enlarged figure of the final position of the boron atom.

The dynamic behavior of the boron implantation process was simulated by our tight-binding quantum chemical molecular dynamics method. Boron atom was bombarded to the surface with initial kinetic energies of 50, 100, and 200 eV. Fig. 4 shows one example of boron implantation process when the boron atom was bombarded with initial kinetic energy of 50 eV. The trajectory of the boron atom is shown in Fig.4 (a) and the final interstitial site occupied by boron atom is magnified in Fig. 4(b). Boron atom was found to have a tendency to diffuse along <110> directions in silicon crystalline by way of hexagonal and tetrahedral interstitial sites. Finally, the bombarded boron atom dominantly occupied the hexagonal site.

Similar calculations were executed from 50 different (x, y) initial positions of boron atoms. 50 simulations from the different initial boron positions were performed for all the initial kinetic energy model of 50, 100, and 200 eV. Less than 50 % boron atoms intruded into the silicon substrate, and others were reflected by the silicon surface. Reflection ratio and average depth of boron atom for each initial kinetic energy are shown in Table 1. It is natural that boron atom with the higher kinetic energy reached to the deeper layer

Table 1 Reflection ratio and average depth of boron atom depending on the initial kinetic energy

Kinetic energy	Reflection ratio	Average depth
50 eV	70.8 %	5.6 Å
100 eV	68.8 %	6.6 Å
200 eV	62.5 %	14.2 Å

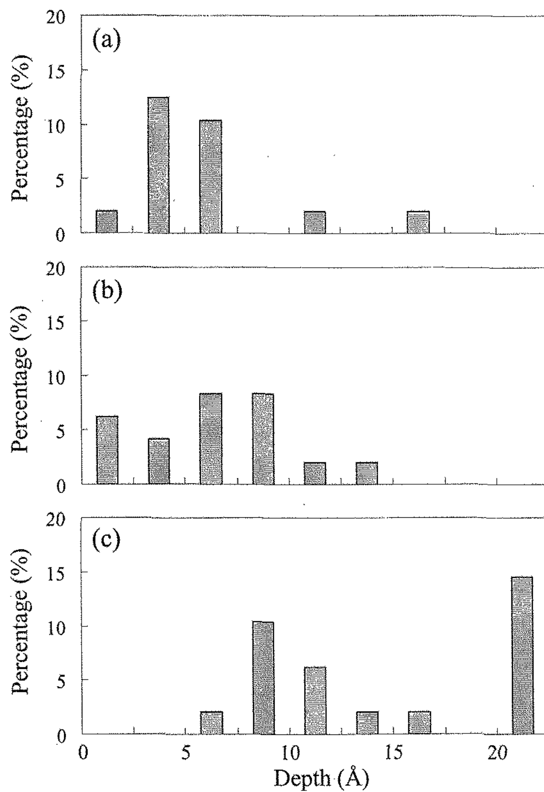

Fig. 5 Depth profile of the boron atom in H-terminated Si(001)2×1 surface for the initial kinetic energy of (a) 50 eV, (b) 100 eV, and (c) 200 eV

and had the lower reflection ratio. Fig. 5 shows the depth profiles of the boron atoms for 50 simulation results. Some boron atoms with the initial kinetic energies of 200 eV penetrated the substrate. The ratio of the boron atoms which reached to the deeper layer than 20 Å, shown in Fig.5 (c) corresponds to these results. This result indicates insufficiency of the thickness of the the silicon substrate model.

We expected that the depth profile of the boron atom can be controlled by the orientation of the boron irradiation, since the boron atom takes selective diffusion path along

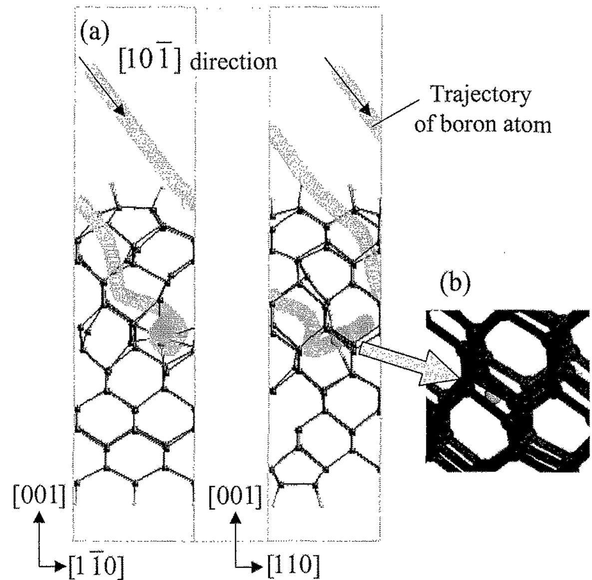

Fig.6 (a) Lateral views of boron implantation process when it was bombarded with initial kinetic energy of 50 eV along [10$\bar{1}$] direction (larger circle indicates boron atom) and (b) enlarged figure of the final position of the boron atom

Table 2 Reflection ratio and average depth of boron atom depending on the incident direction (initial kinetic energy is 50 eV)

Incident direction	Reflection ratio	Average depth
[00$\bar{1}$]	70.8 %	5.6 Å
[10$\bar{1}$]	56.3 %	8.6 Å

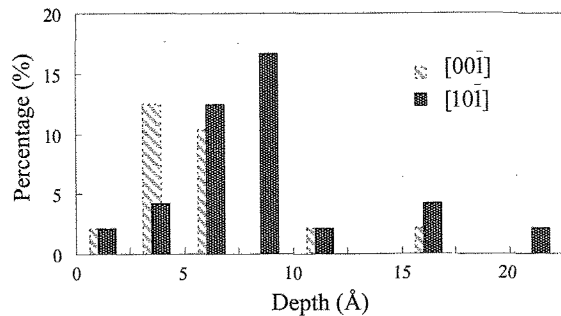

Fig. 7 Depth profile of the boron atom in H-terminated Si(001)2×1 surface depending on the incident direction (initial kinetic energy is 50 eV)

<110> direction. Therefore, we simulated the boron implantation process in $[10\bar{1}]$ direction with initial kinetic energy of 50 eV. Here we employed $[10\bar{1}]$ direction to the Si(001) surface as an irradiation direction among several equivalent <110> directions. Fig. 6 shows one example of the boron implantation process when the boron atom was bombarded with initial kinetic energy of 50 eV along $[10\bar{1}]$ direction. Finally the boron atom was found to occupy hexagonal site. Reflection ratio and average depth of the boron atom depending on the incident direction are shown in Table 2. Fig. 7 shows the depth profiles of the implanted boron atom for 50 simulation results. These results indicated that boron atom, which bombarded along $[10\bar{1}]$ direction, reached to the deeper layer and had the lower reflection ratio than that along $[00\bar{1}]$ direction with the same initial kinetic energy. Therefore, these results suggest that the depth profile of the implanted boron atoms can be controlled by the orientation of boron irradiation.

4. CONCLUSION

In the present study, we successfully simulated low energy boron implantation process into silicon surface by using our original tight-binding quantum chemical molecular dynamics program. The reflection ratio and depth profile of the implanted boron atom were found to depend strongly on the initial kinetic energy and incident direction. Our simulation results suggest that the depth profile of the implanted boron atoms can be controlled by the orientation of boron irradiation. Finally, we concluded that our tight-binding quantum chemical molecular dynamics method is very effective tool to analyze the dynamic behavior of the boron implantation process, considering the chemical reaction and electronic state.

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