Computer Simulation of Decaborane Implantation and Rapid Thermal Annealing

Zinetulla Insepov, Takaaki Aoki, Jiro Matsuo, and Isao Yamada
Ion Beam Engineering Experimental Laboratory, Kyoto University,
Sakyo, Kyoto 606-8501, Japan
e-mail: insepov@kuee.kyoto-u.ac.jp

Abstract - Molecular Dynamics (MD) and Metropolis Monte-Carlo (MMC) models of monomer B and decaborane implantation into Si and following rapid thermal annealing (RTA) processes have been developed. The implanted B dopant and Si-atomic diffusion coefficients were obtained for different substrate temperatures. The simulation of decaborane ion implantation has revealed the formation of an amorphized area in a subsurface region, much larger than that of a single B^+ implantation, with the same energy per ion. The calculated B diffusion coefficient has values between 10^{-12}-10^{-10} cm^2 s^{-1} which agrees well with experimental values obtained for an equilibrium B dopant in Si. Our calculations have shown an unusual temperature dependence with two different activation energies. Low activation energy, less than 0.2 eV, was obtained for a low-temperature region, and a higher activation energy, ~ 3 eV, for a higher-temperature region which is typical for the RTA processing. The higher activation energy is comparable with the equilibrium activation energy, 3.4 eV, for B diffusion in Si. The diffusivity for Si atoms was obtained to be in the interval 10^{-14} - 10^{-12} cm^2 s^{-1}. In our present simulation for decaborane cluster implantation into Si, we have not observed the TED phenomenon.

I. Introduction

Implanted B dopant diffusion in Si has recently attracted much attention because of the anomalously high diffusion rate, the TED effect [1], which has been revealed when heavily doped Si samples were rapidly thermally annealed at a temperature of about 800 - 1000 °C for 10s. (RTA). The realistic physical model of TED has then been proposed stating that every implanted B^+ ion creates at least one Si-interstitial (the so called +1 model), and that the highly migrating B interstitials are due to the kick-out mechanism caused by the Si self-interstitials [2].

Decaborane ion, $(B_{10}H_{14})^+$, implantation has been experimentally shown to be a promising new technique for future small scale PMOS devices. Very shallow junctions have been obtained with low-energy decaborane implantation into a Si surface [3].

Dopant diffusion in Si is a well studied area of semiconductor physics [4-10]. Modeling of low energy decaborane implantation has attracted much less attention so far compared with that of single B^+ ion implantation. To the authors' knowledge, there has been simulation of 1.5 and 4 keV decaborane implantation into a Si substrate with Molecular Dynamics [11]. Unfortunately, MD predicts positions of dopants and defects for a very small time interval, typically less than 20 ps, which is not long enough to simulate diffusion of B during RTA processing.

The aim of this paper is to simulate decaborane implantation into Si at room temperature and the subsequent RTA process at a much higher temperature, by combination of Molecular Dynamics and Monte-Carlo methods, in a low ion energy implantation region. For comparison, simulation has also been performed for the monomer B^+ ion implantation, with the same dose and same energy per atom, and subsequent annealing.

II. Model

As the B atomic mass makes up only 1/3 of the Si atomic mass, the implanted B atoms undergo rare but violent collisions with neighboring Si atoms. Therefore, the motion of B atoms could not be considered as a Brownian one. This makes finding the B diffusion constant a challenging problem for theory. Molecular Dynamics can in principle find the diffusion coefficient, but it is incapable of treating a realistic system for a long computation time. This is usually limited to tens of ps which is not long enough to simulate diffusion of B during RTA processing.

On the other hand, the kinetic models using rate equations for defect concentrations, are rather insufficient for the real three-dimensional modeling of decaborane implantation. This follows because the space scale of averaging in this technique is much larger than that in the decaborane case, due to a higher non-uniformity of dopant distribution.

As RTA is usually applied for 10s, a time scale which too long for a MD method, a method combining MD with MMC is developed in this paper. As we discuss further, the proposed method could easily extend simulation time up to ~ 1 ms, which is long enough for finding parameters of dopant diffusion. To the authors' knowledge, the MMC has not been used before for obtaining diffusion characteristics of dopants in Si for the ion implantation process of interest.

III. Molecular Dynamics

The atomic positions at monomer ion and decaborane implantation were obtained by the Molecular Dynamics simulation at room temperature. The decaborane molecule was modeled with a B_{10} cluster bombarding a Si substrate. The basic cell size for the MD simulation was determined from the cluster energy between 2 - 5 keV and experimental dose of 10^{13} ion/cm^2 [3]. A cubic slab consisting of about 32,000 Si atoms was used for one decaborane ion impact or for 10 implanted B^+ ions at an energy of 230 eV/atom. For the 5 keV decaborane implantation simulation, a parallelepiped

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containing of about 10^5 Si atoms was used. The periodic boundary conditions (PBC) were used in x and y directions, and Langevine forces were applied to 4 atomic layers, in order to keep the system at a desired temperature. Atoms in the two bottom atomic layers were fixed.

The ZBL potential at short distances combined with the Stillinger-Weber potential at equilibrium distances was used to evaluate interactions between two and three Si atoms, as usual [12]. Interaction between B and Si atoms was modeled via the ZBL screened Coulomb potential at short distances, $r < r_1 = 0.52$ Å, and with a Morse-type potential at long distances, $r > r_2 = 0.86$ Å, as recommended in [11]. The binding energy of B in the Si lattice was used as an adjustable parameter with values between 0 to 1.5 eV. Interaction between two B dopants were modeled with an (exp-6)-type potential, with the depth of 0.2 eV, $r_{eq} = 1.5$ Å.

After of about 200,000 MD-steps for simulation of the first, implantation stage, at room temperature, a constant T, constant P Molecular Dynamics [12] was used to maintain a desired annealing temperature between 100 and 2000K, in order to model the following RTA. This second MD simulation was continued up to 5 ps.

The experimental values for total decaborane cluster energies were 3 and 5 keV in [3]. In this paper we have simulated the implantation of 2.5 and 5 keV decaborane ions because of our interest in modeling very shallow *pn*-junction formation.

In MD simulation, all B and Si atomic positions and velocities are calculated as output data. A distribution of displaced Si atoms, with potential energies > 0.2 eV than average potential energy, as well as other defects can be obtained from the MD result.

In addition, the structure of the irradiated Si substrate was studied by the radial distribution function, *rdf*, for the heavily disordered area of decaborane impact.

The decaborane implantation results were compared with simulation of B^+ ion implantation, with the same dose and same energy per atom.

It should be noted that the calculation of the annealing temperature was an important detail of the proposed method. As we have found in this paper, the accuracy of our diffusion coefficient calculation was determined primarily by the accuracy in finding the temperature within the MD. A constant temperature and constant pressure MD was realized for the system with PBC by scaling all the length variables according to the algorithm in [13].

A large amorphized pocket is obtained directly under the surface. Fig. 1 represents a comparison of radial distribution functions (rdf) for different areas of irradiated and non-irradiated Si. The area heavily disordered with 5 keV decaborane implantation (line *1*) has an rdf which contains a glass peak at ≥ 3 Å. The number of Si atoms having more than 5 nearest neighbors was about 2180 in this case. A lower glass peak was revealed when implanted decaborane had lower energy, 2.3 keV (line *2*). An outer substrate region,

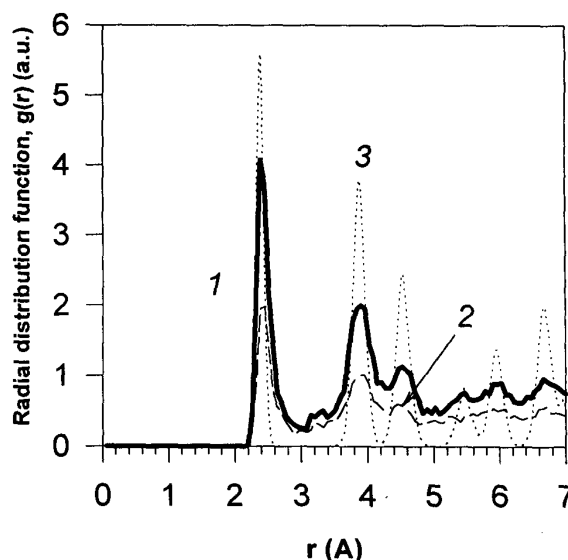

Fig. 1 Radial distribution functions for decaborane implantation into Si obtained after 8 ps MD simulation: *1* - for 5 keV decaborane implantation energy (solid line), *2* - 2.3 keV (dashed line), 3 - the rdf for crystalline areas of the substrate (dotted line).

which was not disordered with cluster implantation, has an rdf which is typical for an ideal crystalline structure (line *3*).

The same simulation of B^+ implantation has shown that there are almost no amorphized areas in the Si substrate.

IV. Monte-Carlo

The atomic positions obtained with the MD were transferred into a Monte-Carlo code for which the Metropolis Monte-Carlo (MMC) algorithm was used [13,14]. In the MMC method, every atomic position of the studying system is displaced within some small increment which can be obtained from the virial expression for a given temperature.

The following initial increments were obtained for B and Si atoms to be satisfactory for a sufficiently short computation time, together with keeping acceptable computation accuracy: $\Delta_B \sim 0.3$ x $(T_{ref} / 300\ K)^{1/2}$, $\Delta_{Si} \sim 0.3$ x $(T_{ref} / 300\ K)^{1/2}$, where T_{ref} =100-2000K.

Actually, the initial values of the increments are not so important because the MMC algorithm adjusts them itself keeping the acceptance probability to be around 0.5. When the initial displacement increment for Si atom was varied from 10^{-7} to 0.01 σ, i.e. within of 5 orders of magnitude, the B diffusion constant only increased by 50%. Here, σ = 2.0951Å.

Fig. 2a shows the results obtained in this paper for the time dependence of the atomic hopping lengths, for B atom - Δ_B (line *1*), and for disordered Si atoms - Δ_{Si} (line *2*). The average value for the Si hopping parameter is 3 times lower than that of B one. The Si hopping range corresponding to well cristalline areas was negligible small.

Fig. 2b shows the time dependence of the B and Si mean-square-displacements in the *xy*-plane: $<\Delta x^2> + <\Delta y^2>$

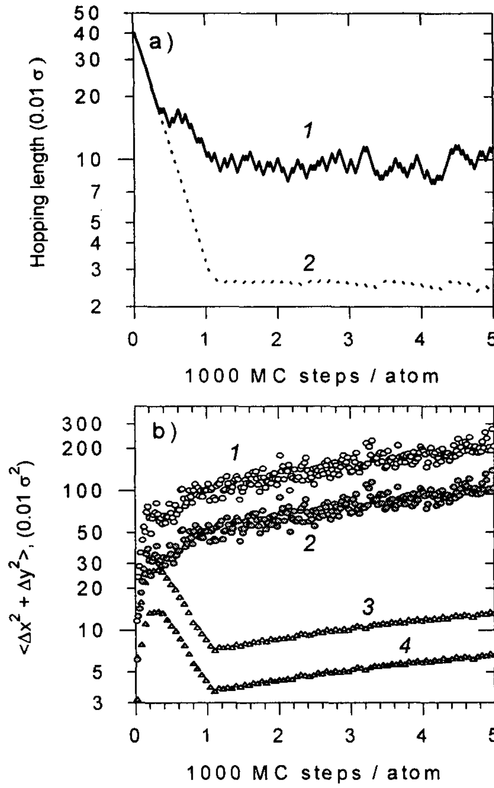

Fig. 2a) Hopping lengths for Boron (*1*) and Silicon atoms (*2*).
Fig. 2b) Boron in *xy*-plane (*1*), in z-direction (*2*), and Silicon *xy*-plane (*3*) and *z*-directional (*4*) displacements at 820K for decaborane implantation obtained with 5,000 MC steps/atom in the MMC simulation.

and in the z - direction: $<\Delta z^2>$ for RTA at 820 K obtained with the MMC code after 5,000 Monte-Carlo steps per atom. The units for the displacements are $\sigma^2 \cong 4.4$ Å^2, where σ = 2.0951 Å is the unit length for the Si S&W potential.

In the MMC method, the time variable is usually measured in Monte-Carlo steps per atom, τ_{MC}, and an additional effort should be done to obtain the real time variable [15]. We have obtained the real time t_R by representing the diffusion constant in the Arrenius form:

$$\boldsymbol{D}_i = \boldsymbol{D}_0 \exp\left(-\boldsymbol{Q}_A / k_B \boldsymbol{T}\right), \qquad (1)$$

where D_i is the diffusion constant of i-th atom, $\{i = \mathrm{B}, \mathrm{Si}\}$, $\boldsymbol{D}_0$ is the pre-exponential which could be estimated as $\boldsymbol{D}_0 \sim \Delta^2\,\nu$, Δ is the average hopping length, and ν is the frequency. $\boldsymbol{Q}_A$ is the activation energy, $\boldsymbol{k}_B$ is the Bolzmann constant, and $\boldsymbol{T}$ is the system absolute temperature. Using the standart logarithmic representation {log$\boldsymbol{D}$ vs $1/\boldsymbol{T}$}, the real time variable t_R could be obtained.

To obtain a diffusion constant in the MMC method, we have calculated the B and Si atomic displacements at different substrate temperatures between 100 and 2000K. The diffusion constant $\boldsymbol{D}_i$ can be calculated directly from the mean-square displacement of a B or Si particle after averaging displacements over all atoms:

$$\boldsymbol{D}_i = \lim_{t \to \infty} \frac{\langle \Delta \boldsymbol{r}_i^2 \rangle}{6\boldsymbol{t}}, \qquad (2)$$

where $<\Delta \boldsymbol{r}_i^2>$ is the mean-square-displacement (MSD) of the particle i $\{i = \mathrm{B}$ or Si$\}$ at time t from its initial position at time 0. We have separated the MSD into two parts: the first one corresponded to the xy-plane displacements $<\Delta x^2>$ + $<\Delta y^2>$ and the second to the z-direction: $<\Delta z^2>$.

The B and Si diffusion constants can be calculated from the slopes of these displacements according to formula (2).

The equilibrium B diffusion constant can be obtained from experiment [3] in the following form:

$$\boldsymbol{D}_B = 0.728 \exp\left(-3.94553 * 10^4 / \boldsymbol{T}\right) + 0.23 \exp\left(-3.94553 * 10^4 / \boldsymbol{T}\right) \qquad (3)$$

where D_B is measured in cm^2 s^{-1}, and T in K. The first term gives the diffusion of neutral B atoms, and the second term that of charged B ions.

A typical evolution of B trajectories during the MC simulation shows that the displacements in xy-plane and in z-direction are almost the same. This means that no predominant diffusion is observed in one direction, for example in the z-direction. The dopant particles continued to have a non-uniform distribution in space during a whole annealing time interval.

This is a pure geometric effect, caused by a non-uniform initial dopant distribution. It might support the idea that at decaborane implantation B diffusion will be 1/3 of that of single B^+ ion implantation, at least during some noticeable part of annealing time. This non-uniformity effect must be significant for cluster ion doses less than 10^{13} cm^{-2}. At higher decaborane implantation doses it should be negligible.

Our simulations did find a small surface effect showing that B atomic trajectories are attracted to and then trapped on the surface, but this effect seems not to be very strong.

Fig. 3 shows the final result for the B and Si diffusion coefficients obtained by fitting time dependencies of the B mean-square-displacements according to the formula (2) for 2.5 and 5 keV implantation energy. Here curve *1* corresponds to the equilibrium constant obtained with formula (3), curve *2* - is the Si diffusion coefficient for a widw range of temperatures. The Si atoms were taken within the area heavily disordered by implantation. Curve *3* - the B diffusion coefficient. The unusual feature of this figure is that it shows two different types of activation processes for the B_{10} cluster

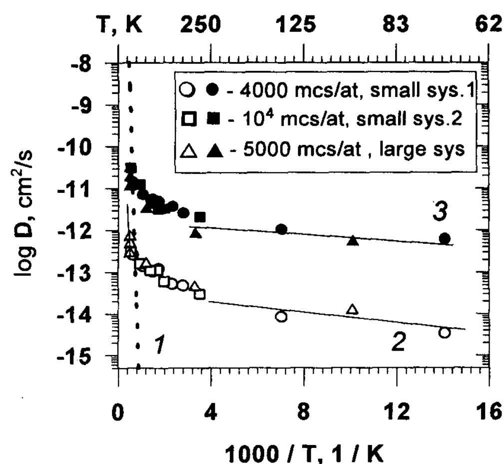

Fig. 3 Boron and Silicon diffusion coefficients obtained with the MC simulation for 2.5 and 5 keV B_{10} implantation into Si: *1* - experimental data for B diffusivity [5], *2* - the Si diffusion coefficient obtained in this simulation for 2.5 and 5 keV B_{10} implantation (open symbols), 3 - the B diffusion coefficient obtained in this simulation for 2.5 and 5 keV B_{10} implantation (filled symbols)

implantation case: for the high-temperature region the obtained activation energy for B is of about 3 eV, which is close to the equilibrium value 3.4 eV of B diffusivity in Si defined by formula (3). A significant lowering of the activation barrier could be seen for the low-temperature region where this value is less than ~ 0.2 eV.

Compared with the result of the tight-binding MD simulation [9], this lower activation process could be ascribed to the vacancy mechanism of diffusion. Actually we did not find any vacancies outside the amorphized zone, but they could be emitted from the amorphized zone upon annealing. On the other hand, our simulation shows that some B atoms are diffusing primarily near the amorphized zone where the definition of a vacancy becomes dubious. Some B atoms were trapped inside this amorphized pocket. Unfortunately, the B diffusion constant in the amorphous Si is unknown, therefore this question needs a further study.

The high-temperature part of the curve *2* was continued to $1/\boldsymbol{T} = 0$, which gives a measure of the Monte-Carlo step per atom in real time to be: $t_{MC} \sim 10^5/\nu_{Si}$. The frequency of Si thermal oscillations ν_{Si} is unknown, we can roughly estimate it to be in the interval 10^{13} - 10^{12} s^{-1}. This estimation gives for the MC-time step $t_{MC} \sim 10^{-8}$ - 10^{-7} s which makes it possible to model the RTA process, with the duration of ~ 10 s.

The Si diffusion constant shown in Fig. 3 was found similar to that of B, and it corresponds to the diffusivity of disordered Si atoms. The Si diffusion constant for the well crystallized areas is much smaller than that of disordered areas, and it needs a separate study.

V. Conclusions

Molecular Dynamics and Metropolis Monte-Carlo models of B cluster and B monomer ion implantation into Si substrate were developed which allow simulation of implantation and subsequent rapid thermal annealing processes in one program as long as a real RTA process requires.

A large amorphized area directly beneath the Si surface was obtained when this substrate was implanted with a B_{10} cluster. The B atoms are mostly stopped within this amorphized area. Compared to that, monomer implantation shows much fewer displaced atoms which are scattered more uniformly in the substrate.

Very good agreement was obtained between calculated and experimental equilibrium B diffusion coefficient at temperatures typical for the RTA. We did not find any TED in our simulation of decaborane implantation into Si, with cluster energies of 2.5 and 5 keV, and B doses of 10^{14} cm^{-2}, at the RTA temperatures.

The B diffusion coefficient was obtained possessing two different activation energies: ~ 3 eV which is close to the equilibrium B activation energy for lightly doped Si, for a higher temperature region, T > 700 K, and a very low activation energy, less than 0.2 eV, for the lower temperature region.

The disordered Si atoms have shown diffusion coefficients of the order of 10^{-13} cm^2 s^{-1}, much higher than that of well crystallized regions.

References

1.D.J.Eaglesham,P.A.Stolk,H.-J.Gossman,T.E.Haynes,J.M.Poate, NIM B **106**, p.191 (1995)

2. E.Chason, S.T.Picraux, J.M.Poate et al., Appl.Phys.Reviews **81**, p. 6513 (1997).

3.I.Yamada, J.Matsuo, E.S.Jones, D.Tekeuchi, T.Aoki, T.Goto, T.Sugii, in Materials Modification and Synthesis by Ion Beam Processing, edited by D.E.Alexander, N.W.Cheung, B.Park, and W.Skopura (Mat. Res. Soc. Symp. Proc. **438**, Pittsburg PA 1997), p.363-374.

4. C.S.Nichols, C.G.Van de Walle, and S.T.Pantelides, Phys.Rev. B **40**, p.5484 (1989).

5.P.M.Fahey, P.B.Griffin, and J.D.Plummer, Rev. Mod. Phys. **61**, p.289 (1989).

6.G.H.Gilmer, T.Diaz de la Rubia, D.M.Stock, M.Jaraiz, Nucl. Instr. Methods B **102**, p.247 (1995).

7..M.Jaraiz, G.H.Gilmer, J.M.Poate, T.Diaz de la Rubia, Appl. Phys. Lett. **68**, p. 409 (1996).

8. S.Tian, M.Moris, S.J.Morris, B.Obradovic, A.F.Tasch, in Materials Modification and Synthesis by Ion Beam Processing, edited by D.E.Alexander, N.W.Cheung, B.Park, and W.Skopura (Mat. Res. Soc. Symp. Proc. **438**, Pittsburg PA 1997), p.83-88.

9. M.Tang, L.Colombo, J.Zhu, T.D. de la Rubia, Phys.Rev. B **55**, p.14279 (1997).

10. P.J.Bedrossian, M.-J.Caturla, and T.Diaz de la Rubia in Materials Modification and Synthesis by Ion Beam Processing, edited by D. E. Alexander, N. W. Cheung, B. Park, and W. Skorupa (Mat.Res.Soc.Symp.Proc. **438**, Pittsburgh PA 1997), p.715-720.

11.R.Smith, M.Shaw, R.P.Webb, M.A.Foad, J. Appl. Phys. **83**, p. 3148 (1998)

12.H.J.C.Berendsen, W.F.Van Gunsteren, In Molecular liquids, dynamics and interaction, edited by A.J.Barnes, W.J.Orville-Thomas, and J.Yarwood (NATO ASI series C135, Reidel, NY 1984) p.475-500

13. D.W.Heerman, Computer simulation methods in theoretical physics, Springer, NewYork, 2nd edition, 1990, pp. 51-103.

14. H.C.Kang W.H.Weinberg, J. Chem. Phys. **90**, p.2824 (1989).

15. P.-L.Cao, Phys.Rev.Lett. **73**, p.2595 (1994).