MD Analyses of Surface Reaction and Adsorbed Free Particle Behavior in LP-CVD Silicon Wafer Processing*

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By using the molecular dynamics method (MD) and computer graphics (CG), the surface processing mechanism of $\text{SiH}_2 \rightarrow \text{Si} + 2\text{H}$ in LP-CVD silicon wafer fabrication is analyzed, in which we introduce a chemical reaction model consisting of the activating energy and attack angle between SiH_2 gaseous molecules and Si atom monocrystalline. The atom surface adsorption and inelastic collision are discussed considering energy exchange between the particles and surface. Moreover, the potential state and behavior of hydrogen atom adsorbed as a free particle are also calculated and discussed. The relevant potential surface of H free particle in the Si crystal lattice is found to be useful to understand its potential state and behavior.

Key Words: Molecular Dynamics, Chemical Reaction, Structural Analysis, Silicon Wafer, LP-CVD, Adsorbed Hydrogen Behavior

1. Introduction

With the development of electronic and computer technologies, better procession control technology of semiconductor wafer processing device becomes more and more important in order to obtain good productivity, high quality and low cost. The technique for low pressure chemical vapor deposition (LP-CVD) of wafer formation has been used extensively because of its extremely favorable economics⁽¹⁾. The microscopic understanding of wafer processing under LP-CVD is essential. Especially, the molecule level analyses of the surface chemical reaction that affects the wafer growth greatly and the optimum control of the surface reaction are thought to be essentially crucial. Furthermore, because the adsorbed free particles during the surface reaction (mainly hydrogen and H-containing reagents)⁽²⁾ are one of the reasons that causes lattice defect and also bring bad influence on

semiconductor properties, it is necessary to understand the behavior of the adsorbed free particles. It is effective to describe such surface process and behavior of free particles by Molecular Dynamics (MD) method at molecular level. However, the MD modeling that considering the reaction has not been well established yet. Moreover, very few study has been reported to identify the existing position of the surface adsorbed free particles according to its potential.

The study analyzes the surface processing mechanism of $\text{SiH}_2 \rightarrow \text{Si} + 2\text{H}$ in LP-CVD silicon wafer fabrication process by MD method and discusses the design of fabricating device with optimum surface reaction control. In the MD model of surface reaction, a new method to judge the chemical reaction considering both the activating energy and attack angle between SiH_2 gaseous molecule and Si atoms monocrystalline is suggested. Moreover, the behavior of hydrogen atom H adsorbed as free particle is also simulated and discussed by MD calculation. It is known that hydrogen (H) and H-containing reagents are widely used in semiconductor technology⁽²⁾, and the specific influence of the incorporated H on silicon material and device properties has been investigated mainly by experimental method⁽³⁾⁻⁽⁷⁾. In this paper, it is shown that the existing position and behavior of the free particle H can be identified according to its potential surface

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shape in the Si lattice.

2. MD Calculation Approach and Surface Reaction Model

Figure 1 shows the SiH₂/Si crystal surface system which is targeted in this MD calculation. The silicon atoms are distributed in three layers of diamond crystal lattice⁽⁸⁾ with the Miller index <111>. The distances between three layers from the surface are 0.78 Å, 2.35 Å and 0.78 Å, respectively. The gaseous SiH₂ molecule is colliding toward the substrate of the Si crystal where the surface reaction processing is discussed according to the following thermal decomposition reaction

where Q is the energy necessary for the reaction. In this calculation, Q values about 2.4×10^{-19} J⁽⁹⁾. The behavior of each particle i of the Si atomic system which is composed of the SiH₂ incidence molecule and the substrate can be calculated according to the following Newton equation of motion under the assumption that the quantum effect is negligible.

$$\frac{d^2(m_i \mathbf{r}_i)}{dt^2} = \mathbf{F}_i = - \sum_{j \neq i} \frac{\partial \Phi(\mathbf{r}_{ij})}{\partial \mathbf{r}} \quad (2)$$

The incident gas molecule SiH₂ is set to start from the upper boundary of the simulation field (15 Å from the surface). The initial position is random decided. The initial translation kinetic energy and the incident angle of the gas molecule are given based on the random number obeying the Maxwell distribution. In the MD method, the model of potential $\Phi_2(\mathbf{r}_{ij})$ in Eq. (2) is important. Here, Lennard-Jones (L-J) potential model is used as the potential between the neutral particles such as SiH₂ and Si and 2H and Si.

$$\Phi(\mathbf{r}) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \quad (3)$$

The value of ϵ and σ which is the L-J potential parameter between SiH₂-Si and H₂-Si adopted by this MD calculation is indicated in Table 1⁽¹⁰⁾. Because of the covalent bond among the silicon atoms, the following Stillinger-Waber (S-W) potential model⁽¹¹⁾,

$$\Phi = \sum_i \sum_{j < k} \Phi_2(\mathbf{r}_{ij}) + \sum_i \sum_{j < k} \sum_l \Phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \quad (4)$$

Fig. 1 SiH₂/Si surface system

where

$$\Phi_2(\mathbf{r}_{ij}) = \epsilon f(\mathbf{r}_{ij}/\sigma) \quad (5)$$

$$\Phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \epsilon g\left(\frac{\mathbf{r}_i}{\sigma}, \frac{\mathbf{r}_j}{\sigma}, \frac{\mathbf{r}_k}{\sigma}\right) \quad (6)$$

$$f(x) = \begin{cases} A \left(\frac{B}{x^p} - \frac{l}{x^q} \right) \exp\left(\frac{l}{x-a}\right) & x < a \\ 0 & x \geq a \end{cases} \quad (7)$$

$$g(x_i, x_j, x_k) = h(x_{ij}, x_{ik}, \theta_{jik}) + h(x_{ji}, x_{jk}, \theta_{ijh}) + h(x_{ki}, x_{kj}, \theta_{ikj}) \quad (8)$$

$$h(x_{ij}, x_{ik}, \theta_{jik}) = \begin{cases} \lambda \exp\left(\frac{\gamma}{x_{ij}-a} - \frac{\gamma}{x_{ik}-a}\right) \left(\cos \theta_{jik} + \frac{1}{3}\right)^2 & x_{ij} < a \text{ and } x_{ik} < a \\ 0 & x_{ij} \geq a \text{ or } x_{ik} \geq a \end{cases} \quad (9)$$

which takes both two-body $\Phi_2(\mathbf{r}_{ij})$ and three-body $\Phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ potentials, respectively, into account is used. Table 1 shows the potential parameters being applied⁽¹²⁾. In this case, the force $\mathbf{F}_i$ on particle Si according to S-W potential turns to be

$$\mathbf{F}_i = - \sum_{j \neq i} \text{grad } \Phi_2(\mathbf{r}_{ij}) - \sum_{j < k \neq i} \text{grad } \Phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \quad (10)$$

The chemical reaction of Eq.(1) takes place when the following two requirements are satisfied. The first one concerns on the reaction energy. Only when the collision energy of incident molecule SiH₂ with surface $E_{\text{SiH}_2\text{-Surface}}$ is larger than the necessary energy $E_{\text{SiH}_2} = 2.723 \times 10^{-19}$ J to cut off the SiH₂ internal bonding, i.e.,

$$E_{\text{SiH}_2\text{-Surface}} > E_{\text{SiH}_2} \quad (11)$$

The second condition concerns on the acting angles of reactive particles' space distribution. The interaction angle $\theta_{\text{SiH}_2\text{-Surface}}$ between the SiH₂ center axle and the surface should be less than the reaction critical angle θ_{crit} , i.e.,

$$\theta_{\text{SiH}_2\text{-Surface}} < \theta_{\text{crit}} \quad (12)$$

In this calculation, as the first approximate, $\theta_{\text{crit}} = 45^\circ$ is used. The reason locates on the results of our MO reaction analyses that the center collision ($\theta = 0$) has the highest possibility of reaction⁽¹³⁾, and mainly the reaction happens under $\theta < 45^\circ$. Only when the incident molecule SiH₂ satisfies the above two conditions (11) and (12), the reaction Eq.(1) happens. SiH₂ is decomposed into Si and two hydrogen. The Si moves around the surface (mobility movement) while losing

Table 1 Interaction potential parameters of L-J and S-W models

Interaction Pair	ϵ [J]	σ [Å]	Others (Non-dim.)
SiH ₂ -Si (L-J)	3.51×10^{-30}	3.50	—
H ₂ -Si (L-J)	1.66×10^{-30}	4.98	—
Si-Si (S-W)	3.4723×10^{-19}	2.0951	$A=7.0496, B=0.6022, p=4, q=0, \alpha=1.8, l=21, g=1.2$

its kinetic energy. Probably it will contribute finally to the wafer growth under the covalent bonding. Most of the H particles will escape from the surface. However, some of them become free particles wandering on the surface and adsorbed by the surface which is thought to be impurity for the device.

In this MD calculation, the substrate temperature of the Si crystal surface is set to be constantly 600 K and the period boundary condition is applied to the area that exceeds the diamond structure (lattice spacing $3.13\text{\AA}$) in the calculation area on the surface shown in Fig. 1. For one state parameters, the calculation will be repeated for about 50 times and their average will be treated as the result of that state. One time calculation includes maximum 40 000 steps. The details of the calculation processing is shown in Ref. (8).

3. Results and Analyses of Surface Reaction

3.1 Behavior of incident particle SiH_2

Figure 2 shows two typical examples of the SiH_2 gaseous molecule's behavior near the surface. In Fig. 2(a), the incident molecule SiH_2 and the Si surface state don't meet the conditions Eq.(11) and (12). The incident molecule is first accelerated and approaching the surface under the action of potential energy. After several times collision against the surface, the energy exchange with the surface is completed and then escapes from the surface while being decelerated.

(a) without reaction ($V_z = 4.5\text{\AA}/\text{ps}$).

(b) with reaction ($V_z = 5.1\text{\AA}/\text{ps}$).

Fig. 2 Behavior of intrusion particle SiH_2

The case in Fig. 2(b) shows that the surface reaction conditions Eq.(11) and (12) are satisfied and the atom Si obtained from the decomposed reaction loses its energy gradually and turns to be the same level as the surface crystal atoms. Finally it remains on the surface as a new part of the surface structure while the hydrogen atoms escape from the surface according to the potential force from the surface.

Figure 3 shows the examples of the potential time-variation process of gas molecules SiH_2 without decomposition reaction which is responding to Fig. 2(a). Under the case with incident velocity $V_z = 4.5\text{\AA}/\text{ps}$, we can observe the typical scattering process. First, the approaching SiH_2 molecule is accelerated by the potential from the surface Si atoms. In this stage, the gas molecule loses its potential energy $\langle PE \rangle$ and obtains the kinetic energy $\langle KE \rangle$ in exchange. Next, from the time t_1 to t_2 , it is called as the energy transferring stage. At this stage, the gas molecule loses its kinetic energy and obtains the potential energy in return. For case (a), the gas molecule owns enough total energy $\langle TE \rangle$ at time t_2 to go through the L-J potential-well energy ϵ , and then escapes from the surface. On the other hand, with the incident velocity $V_z = 4.0\text{\AA}/\text{ps}$ of the gas molecule in case (b), the total energy after the energy transferring stage is less than the potential-well energy, i.e., $\langle TE \rangle_{\text{SiH}_2} < \epsilon$. In this case, the potential energy of the gas molecule Si increases while receiving the repulsive force from the surface. Its kinetic energy decreases. Different from case (a), its potential energy turns to

Case (a): $\langle TE \rangle_{\text{SiH}_2} > \epsilon$.

Case (b): $\langle TE \rangle_{\text{SiH}_2} < \epsilon$.

Fig. 3 Time history of SiH_2 energy without reaction

decrease again (kinetic energy increases) according to the surface Si potential and it approaches the surface repeatedly instead of escaping. From time t_1 with the initial minimum potential energy, the gas molecule keeps moving back and forth near the surface and is trapped by the surface at last. Such trap is different from real adsorb. It still keeps mobility wandering within certain area. It is the mechanism of physical adsorption and such adsorption phenomenon is thought to hamper other particles' interaction with the surface and be blight to high quality silicon wafer formation. The increase of the energy of the inlet gas or the temperature of the substrate is proposed to avoid such physical adsorption phenomenon.

3.2 Surface reaction process

Figure 2(b) is the example of the case that meets the reaction conditions (11) and (12), and surface reaction (1) happens. Figure 4 shows an example of the potential energy $\langle PE \rangle_{\text{SiH}_2}$ and total energy $\langle TE \rangle_{\text{SiH}_2}$ time-variation processes of a gas molecule SiH_2 with the decomposition reaction. In Fig. 4, time t_c indicates the time that surface reaction happens. The first stage before the reaction $t < t_c$ has the same energy variation shape as in Fig. 3. However, at time $t = t_c$, the decomposition reaction (1) of the gas molecule SiH_2 takes place on the surface and is decomposed into Si and 2H with different potential energy. For 2H, it continues the energy exchange stage and escapes from the potential-well at last while being decelerated. As for Si, it is accelerated at first and slows down later according to the S-W potential. Moreover, the Si atom loses its kinetic energy gradually and "melts" into the surface crystal with covalent bond. From the SiH_2 total energy $\langle TE \rangle_{\text{SiH}_2}$ variation figure, a step-up phenomenon at the surface reaction time is observed which is known to be equivalent to the reaction energy Q .

4. Calculation Results and Analyses of Hydrogen Free Particle Behaviors

4.1 Simulation model and calculation method

It is industrially important to understand the behavior and final stopping position of the hydrogen atom generated from the surface reaction discussed in Chapter 2 as a free particle moving around the crystal surface because it may be the cause of wafer lattice defect and bring bad effect on the wafer productivity. However, the behavior of a free hydrogen particle in the silicon wafer of the diamond structure has not been well elucidated though a lot of researches concerning on this field are reported⁽⁶⁾.

The model chosen for the MD analyses is based on a cluster of 14 Si atoms centered around a hexagonal interstitial site P_{Hex} as shown in the model crystal

Fig. 4 Time history of a SiH_2 potential with reaction

Fig. 5 Model crystal consisting of 14 Si atoms in a cubic

(Fig. 5), which is terminated by 20 surfaces. In the figure, P_{Td} is the tetrahedral interstitial site which usually is quoted as the potential minimum for H in a perfect Si lattice. Point P_C is the center site of the rhombus shown in the figure.

In the MD calculation, the initial distribution of free particle atom H is randomly placed that is a little far away from P_{Hex} , P_{Td} and P_C to reduce surface potential effects.

The total energy of the model crystal is calculated with atomic H as a function of its position in the Si lattice and referred to henceforth as the H potential. To understand the state and stability of H atom in Si lattice, no kinetic energy is taken into account here because the velocity of the atom H under adsorbed state is relative low. In the calculation, the potential models L-J and S-W which are discussed in Chapter 2 are adopted. The behavior of the free hydrogen particle H in the silicon cluster obtained by the MD calculation and its final stopping position are examined by its potential.

4.2 Calculation results and analyses

The potentials of the atomic free particle H in Si lattice along some major axes, i.e., $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$, are shown in Fig. 6. The abscissa shows the existing position of H. Along the axle $\langle 111 \rangle$, point P_{Hex}

Fig. 6 Potentials of H in Si lattice along $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ axes

is set to be the central point while points P_C and P_{Td} for axes along $\langle 110 \rangle$ and $\langle 100 \rangle$, respectively.

Along $\langle 111 \rangle$ axis point P_{AB} on abscissa indicates an antibonding site with a local minimum at a distance of $1.6 \text{ \AA}$ from the Si atom in the crystal model. It can be understood that along $\langle 111 \rangle$ direction there exists a local minimum at the antibonding position P_{AB} while both P_{HeX} and P_{Td} showing local maximum potential of H atom. There exist four sites with local minimum potential along $\langle 111 \rangle$ direction where the H atoms are easy to stay around.

If we observe the H potential along the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions, a minimum near the point P_C can be

Fig. 7 Potential map of H on Si(110) plane

found, which is much lower than the minimum at point P_{AB} of $\langle 111 \rangle$ direction. The difference may reach 1 eV according to the simulation. The geometry of point P_C in the Si lattice can be visualized as the center of the rhombus formed by three connected Si atoms and the P_{Td} site (refer to Fig. 5). It is shown from Fig. 6 that H potential near point P_C is considerably lower than point P_{AB} of $\langle 111 \rangle$.

By moving an H atom around the Si(110) plane, the potential map of the H atom on Si(110) plane is obtained as shown in Fig. 7. According to this potential map, it is easy to understand the state and behavior of H atoms in silicon wafer crystal. Based on the potentials of different planes as shown in Fig. 7, the main potential minimum (-1616.04 eV) is determined to be located at the P_M site, which is defined as the middle point between two nearest P_C along $\langle 100 \rangle$ in Fig. 5. The distance between an H located at P_M and two nearest Si atoms is equal to $1.52 \text{ \AA}$. They form something like a three-center bond⁽¹⁴⁾. Its position is located on plane Si(440). The free particle H first tends to saturate the dangling bonds at defect sites such as P_C and P_M . As a result, certain Si-H bond with the lowest energy ($-14.0 \text{ eV} \sim -15.8 \text{ eV}$) is formed. Moreover, it is possible for one H atom to migrate from one equilibrium site P_M to another across site P_C . The potential barrier between them is very small, as about 0.32 eV . Therefore, it can be understood that the movement of the hydrogen atom

as a free particle can happen comparatively easy.

As mentioned above, the equilibrium position P_M of atomic H in c-Si wafer with diamond structure is located at the middle point between two adjacent sites P_C along $\langle 100 \rangle$, which in turn is the center of a rhombus formed by three connected Si atoms and the nearest site P_{Td} shown in Fig. 5. Si atoms and point P_{Td} together with H atoms at sites P_C form a simple cubic lattice. The distance between point P_M and two nearest Si atoms is equal to 1.52 Å. The elements of the bond-order matrix corresponding to the hydrogen atom show that at the site P_M a three-center bond is formed by the free particle H and its nearest two Si atoms.

5. Conclusion

The surface reaction ($\text{SiH}_2 \rightarrow \text{Si} + 2\text{H}$) when making silicon wafer through LP-CVD process is simulated by MD method. Two judgment conditions concerning both the bond energy and the interaction angle are introduced as reaction critical conditions. According to the simulation results of the crystallization process under the LP-CVD state, the procedure can be divided into three steps. The first stage is the acceleration one in which the kinetic energy of the incident gas molecule increases with time. The second stage is called as the reaction one where the energy is transferred between the gas molecule and the surface, and it results in the new molecule and/or atom generation. As for the third stage, we call it as the relaxation in which the new crystal lattice is formed accompanying an attenuation vibration at the lattice-site. The mechanism of physical adsorption that non-reaction gas particles move around the surface while losing their energy is elucidated.

The potential calculation of hydrogen atom H is conducted within a cluster crystal model formed by 14 Si atoms to understand the behavior and final stopping position of the free hydrogen atoms generated by the surface decomposition reaction. The hydrogen atom

bonded to a Si atom at the defect sites saturating a dangling bond Si-H has the lowest potential energy. The atomic hydrogen as free particle holds the equilibrium position at point P_M with the main minimum potential value. It is interesting to notice that such equilibrium position with the main minimum potential value is different from the ordinary imagination of site P_{AB} or P_{Hex} . Moreover, these configurations of hydrogen in c-Si structure are dynamically in equilibrium among themselves.

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