

The development of molecular dynamics potential for an Si-H system and its application to the translationally activated CVD process

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Summary

In order to investigate the reaction probability of silane dissociative adsorption, we developed a new Si-H potential. By using molecular dynamics with our potential, the dependence of the molecular and substrate temperatures on the reaction probability was investigated and was compared the results with the translationally activated process.

Introduction

Recent research in the field of semiconductors has attempted to apply the atomic simulation to next generation process simulation. Chemical vapor deposition (CVD) from silane (SiH_4) is widely used as a technique for silicon film growth, and is one of the fields in which we expect to find many applications of the atomistic approach. The first step of the growth process is the adsorption of the silane to the silicon surface, and many studies have shown that the growth rate depends on surface hydrogen coverage, surface temperature, silane energy and surface orientation[1][2][3]. The adsorption step on the Si(100)-(2×1) surface may be regarded as $\text{SiH}_4(\text{g})+2\text{-} \rightarrow \text{H} + \text{SiH}_3$, where - indicates a surface active site (dangling bond). Gates et al.[1] found that the probability of dissociative adsorption on a clean Si(100) surface was 3×10^{-5} (silane: room temperature; substrate: 673K) and that the activation energy derived from the surface temperature dependence was 3kcal/mol (0.13eV)[2]. However, the reaction probability (P_r) at low temperatures is too small despite the low activation energy. To explain this paradox, Gate et al.[1] suggest that P_r was significantly more dependent on the internal energy of the silane than on the substrate temperature and that the specific degree of freedom of the silane must be excited in order to reach the transition state. Brown et al.[4] theoretically found the activation energy of dissociative adsorption of silane by first-principle calculation using the density functional method. The energy barrier for this reaction was predicted to be 12-14 kcal/mol (0.52-0.61eV), which differed from the results obtained in the experiment; Brown et al. therefore consider that the actual energy barrier was much higher than the apparent activation energy obtained from only surface heating. Jones et al.[5] explored experimental methods of examining the influence of the silane internal energy. They showed that P_r scaled exponentially with the normal component of the translation energy E_{\perp} and that P_r is not dependent on nozzle temperature (vibration temperature) from their translationally activated process. Brown et al. proposed that SiH_4 react with internal excitation, and that the particular type of internal excitation required for reaction was not enhanced by nozzle heating. That is, the excitation of some special modes is necessary for the reaction, which is likely to result from collision with the surface. Since the dissociative adsorption of silane cannot be described by simple thermal activation theory, approaches based on dynamics are necessary to investigate the effects of the translation and vibration energy of silane as well as substrate temperature.

In this study, we used classical molecular dynamics assuming the empirical potential to evaluate these dynamic effects on P_r . We then compared our results with those obtained by Jones et al. in their translationally activated experiment. Molecular dynamics potentials for Si-H systems have been proposed by several researchers[6][7]. Because it is difficult to apply these potentials to silane dissociative adsorption, we developed a new Si-H potential for silane dissociative adsorption.

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The development of a molecular dynamics potential for an Si-H system

It generally accepted that, for development of the molecular dynamics potential, the stable cluster and bulk structures must first be reproduced. Energy, bond distance and vibration wave number of silicon hydride clusters of various sizes and geometry (from SiH_x to Si_7H_x) are used for the fitting through which it is possible to produce a simulation in which a small cluster becomes a large cluster. In addition, it is necessary to reproduce the transition state is required in order to deal with the reaction. The activation energies of the silane dissociative adsorption and hydrogen desorption, which are important elementary processes of crystal growth, are fitted.

The form of our potential is based on the Tersoff bond-order potential[8]. The correction functions F_1 , F_2 and H are introduced for the Si-H attractive and repulsive terms (Eq.(2)) as with the Marty-Tersoff potential[6][8], and the correction function G is introduced in the bond-order term (Eq. (3)) for the Si-Si double bond as with the Brenner potential[9]:

$$\Phi = \sum_{i,j} V_{ij} \quad (1)$$

$$V_{ij} = Af_c(r_{ij})F_1^{\text{Si-H}}(N_{si})\exp(-\lambda_A r_{ij}) - f_c(r_{ij})BF_2^{\text{Si-H}}(N_{si})\exp(-\lambda_B r_{ij})\overline{b_{ij}} \quad (2)$$

$$\overline{b_{ij}} = \frac{1}{2} \left(b_{ij} + b_{ji} + G_{ij}^{\text{Si-Si}}(N_i^{\text{tot}}, N_j^{\text{tot}}, N_{ij}^H) \right), \quad b_{ij} = \left(1 + \zeta_{ij}^\eta \right)^{-\delta} \quad (3)$$

$$\zeta_{ij} = \sum_k f_c(r_{ik}) \left[c + d \{ H(N_{si}) - \cos \theta_{jik} \}^2 \right] \exp \left[\alpha \left\{ (r_{ij} - R_{ij}^e) - (r_{ik} - R_{ik}^e) \right\}^\beta \right] \quad (4)$$

$$N_{si} = \sum_{j=H} f_c(r_{ij}) \quad (5)$$

$$N_i^{\text{tot}} = \sum_k f_c(r_{ik}), \quad N_j^{\text{tot}} = \sum_k f_c(r_{jk}), \quad N_{ij}^H = \sum_{k=H} f_c(r_{ik}) + \sum_{l=H} f_c(r_{jl}) \quad (6)$$

where f_c is the cutoff function, N_{si} is the coordination number of the Si atom in the Si-H bond, N_i^{tot} and N_j^{tot} are the coordination numbers of the i th and j th atoms, respectively, and N_{ij}^H is the number of hydrogen atoms in N_i^{tot} and N_j^{tot} . $F_1^{\text{Si-H}}$ and $F_2^{\text{Si-H}}$ are applied only to the Si-H bond, and $G_{ij}^{\text{Si-Si}}$ is applied only to the Si-Si bond. The values of A , B , λ_A , λ_B , η , δ , R , D and R^e depend only on the atoms i , j . The values of α , β , c , d and H depend on the atoms i , j , k .

In developing a highly accurate potential, it is desirable that the potential be fitted to as many clusters as possible. However, since little experimental data on bond distance and energy is available for potential fitting, data collection is of great concern. In this study, the physical properties for fitting were obtained from a Gaussian 98 G2 set calculation[10]. Since G2 set calculation is accurate to within 1.2 percent compared with experiments, it is considered to be sufficient for potential fitting. H_2 and the stable 32 cluster structure from SiH_x to Si_7H_x are selected as fitting clusters, that is 1. H_2 , 2. SiH , 3. SiH_2 , 4. SiH_3 , 5. SiH_4 , 6. Si_2H_2 , 7. Si_2H_4 , 8. Si_2H_6 , 9. HSiSiH_3 , 10. Si_3H_8 , 11. $\text{Si}_3\text{H}_6\text{A}$, 12. $\text{Si}_3\text{H}_6\text{B}$, 13. Si_3H_6^* , 14. $\text{Si}_3\text{H}_4\text{A}$, 15. $\text{Si}_3\text{H}_4\text{B}$, 16. Si_4H_{10} , 17. $\text{Si}_4\text{H}_8\text{A}$, 18. Si_4H_8^* , 19. $\text{Si}_4\text{H}_6\text{A}$, 20. $\text{Si}_4\text{H}_6\text{B}$, 21. Si_5H_{12} , 22. $\text{Si}_5\text{H}_{10}\text{A}$, 23. $\text{Si}_5\text{H}_{10}\text{B}$, 24. $\text{Si}_5\text{H}_{10}^*$, 25. $\text{Si}_5\text{H}_8\text{A}$, 26. Si_6H_{14} , 27. $\text{Si}_6\text{H}_{12}\text{A}$, 28. $\text{Si}_6\text{H}_{12}^*$, 29. $\text{Si}_6\text{H}_8\text{A}$, 30. Si_6H_6 , 31. Si_7H_{16} , 32. $\text{Si}_7\text{H}_{14}\text{A}$, 33. $\text{Si}_7\text{H}_{14}^*$. A and B indicate the group of silene and silylene. * indicates the cyclic form. For these clusters, the fitting parameters are two-body terms of Si-Si, Si-H and H-H (except for cutoff parameters, R , D , R^e

Table 1: Two-body potential parameters of our proposed Si-H potential, *Our fitting parameter, *¹ are same as Marty-Tersoff, *² are same as Brenner

	Si-Si	Si-H	H-H
A [eV]	1830.8* ¹	456.00*	97.25*
B [eV]	471.18* ¹	70.659*	29.695*
λ_A [\AA^{-1}]	2.4799* ¹	3.3935*	4.739*
λ_B [\AA^{-1}]	1.7322* ¹	1.6068*	1.869*
η * ¹	0.78734	1.0	1.0
δ * ¹	0.635	0.80469	0.80469
R [\AA^{-1}]	3.0*	2.25*	1.4* ²
D [\AA^{-1}]	0.2*	0.15*	0.3* ²
R^c [\AA^{-1}]	2.35	1.4824*	0.738*

Table 2: Parameters for collection functions of our proposed Si-H potential

$F_1(1)$	1.0736	$H(1)$	-0.04536
$F_1(2)$	1.0873	$H(2)$	-0.04536
$F_1(3)$	0.93248	$H(3)$	-0.361625
$F_1(4)$	1.0000	$H(4)$	-0.4700
$F_2(1)$	0.95788	$G_{ij}^{Si-Si}(2,2,0)$	0
$F_2(2)$	0.99300	$G_{ij}^{Si-Si}(2,2,1)$	0.352
$F_2(3)$	0.91607	$G_{ij}^{Si-Si}(2,2,2)$	0.100
$F_2(4)$	1.00000	$G_{ij}^{Si-Si}(2,2,3)$	0.100
		$G_{ij}^{Si-Si}(2,2,4)$	0.176

Table 3: Three-body potential parameters of our proposed Si-H potential, *Our fitting parameter, *¹ are same as Marty-Tersoff, *² are same as Brenner

	Si-Si-Si* ¹	Si-Si-H Si-H-Si Si-H-H *	H-Si-Si*	H-Si-H H-H-Si*	H-H-H* ²
α	5.1975	4	2	2	3
β	3	3	1	1	1
c	0	0.0246	1.4	1.1	4
d	0.16	0.4037	0	0	0
h	-0.59826	see Table.3	-	-	-

), and three-body terms of Si-Si-H, Si-H-Si and Si-H-H. Many potential parameter sets are produced using the Monte Carlo method. From these sets, the best parameter set with the smallest error rate was chosen. The results of potential parameters are shown in Tables. 1, 2 and 3. The results of cluster energies are shown in Fig. 1 where we plot the absolute errors against the cluster number shown above. The results obtained with the Marty potential are also shown for comparison. As may be seen, the accuracy of energy is higher than that of Marty. The averaged errors are 1.0% and 3.3%, respectively (note that Marty used different energy values for fitting). The averaged error of vibration wave number of H₂ and SiH-SiH₄ is 7.3% (Marty 7.0%).

In order to fit the transition state of hydrogen desorption, we fit the activation energy of the hydrogen desorption to the experimental value 2.49[eV][11], using the following parameters: Si-H cutoff distance R , D , the three-body terms of H-Si-H and H-H-Si (Table. 2). Following Hansen's assumption[7] that hydrogen moves faster than silicon, the energy of the transition state reaches 2.4 eV. In order to fit the transition state of silane dissociative adsorption, we chose to use the value presented by Brown et al. for the fitting, although the transition state is not yet fully understood. In order to find the transition state, we used a Dual-direction Gradual Ascent (DGA) method which improves on the Gradual Ascent (GA) method proposed by Bulatov et al.[12] by including the dual direction. For fitting, the Si-Si cutoff distance R , D , and the three-body term H-Si-Si (Table. 2) were adjusted by trial and error. The activation energy of the saddle point decreases as the parameter of c is lowered (bond-order increases). The schematics of the initial, transition and final states of dissociative adsorption are shown in Fig. 2. The activation energy and energy difference are also shown. The activation energy of our potential reaches 0.56 eV and agrees with the value obtained by Brown et al. However, the activation energy of intra-row (0.27eV) and inter-low (0.11eV) has become lower than that of intra-dimer because their respective transition states are more similar to their stable states than in the case of intra-dimer.

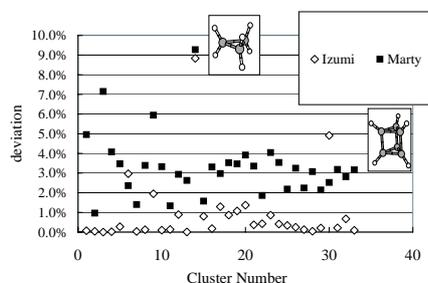


Figure 1: Absolute errors of the cluster energy

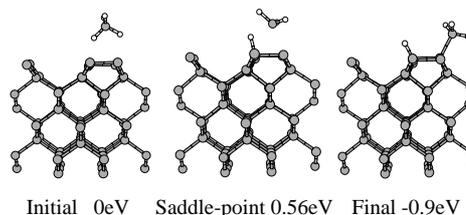


Figure 2: Schematic reaction path for dissociative adsorption of silane.

The calculation model for the reaction probability of silane on silicon surface

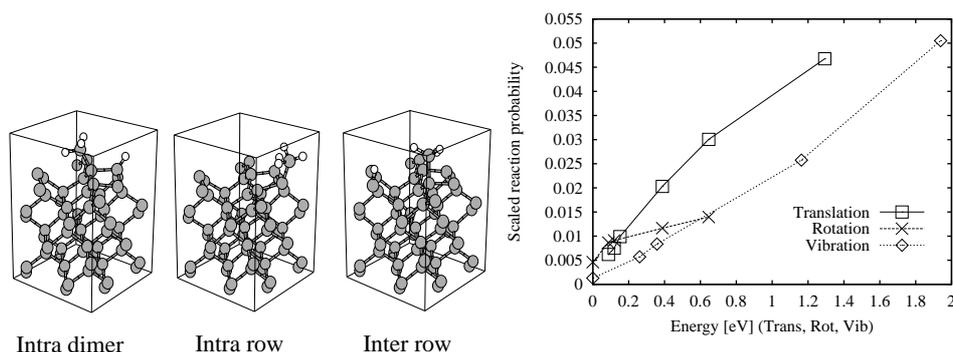
For the calculation of P_r , in general, the silane with internal energy given by the Boltzmann distribution is impacted to the silicon substrate. However, since extensive calculation is necessary for each experiment temperature in this procedure, it is not suitable for the molecular dynamics simulation. In this study, therefore, internal temperatures (translation, rotation and vibration) were scaled to constant values in all trials. We produced the approximation functions based on the table of the scaled reaction probability \hat{P}_r for various combinations of the internal temperatures. We then weighted the integral of the approximation function by the Boltzmann distribution and obtained the true P_r . The calculations at any internal temperature were determined by this method which is considered to clarify the effects of each internal temperature on P_r .

The molecular dynamics simulation employs crystals with 64 atoms, which correspond to a cube of silicon of 10.86\AA on a side. Periodic boundary conditions are applied in the two horizontal (x, y) directions, with a free surface at the topmost (001) plane. The two bottom (001) planes with 16 atoms are held fixed and the next two planes are set to a constant temperature by the scaling method. After the substrate is sufficiently relaxed, silane is collided with the substrate. The condition of the substrate is prepared in 20 types in order to consider the scattering of the vibration of the substrate. The position, orientation and rotation axis of the silane are set to be random. The incident angle is set to be normal to the surface, and the number of trials is set at 20,000 in order to obtain a probability of the order of 10^{-3} . The molecular internal temperature (translation, rotation and vibration) varies between 100K-10000K. We examined the effects of three substrate temperatures (673K, 923K and 1173K). In order to be able to conduct valid comparisons with the experiments of Jones et al.[5], calculations were carried out under the necessary conditions so that P_r of the translationally activated process with 0.4-1eV energy (vibration temperature of about 673K) could be accurately obtained.

The result of reaction probability

The main reaction paths are found at the intra-dimer site (Fig. 3, left), the intra-row site (Fig. 3, middle) and the inter-row site (Fig. 3, right) and chemisorptions of decomposed silane are produced by the collision with the substrate. For example, when the translation, rotation and vibration velocity are set at 3000K, the ratios of the reaction are 12.8, 20.3, 33.0 and 12.3%, respectively, which roughly reflect each activation energy (except for the decomposed reaction). The translation, rotation and vibration energy dependences of \hat{P}_r are shown in Fig. 4 (no correction with the Boltzmann distribution). The other internal temperatures are set at 1173K. \hat{P}_r increases almost linearly with increased

translation energy, but the gradient decreases at a transition energy of over 0.65 eV. Observation of each reaction path reveals that \hat{P}_r of the inter-row site is saturated due to its low activation energy. Vibration energy dependence can be approximated by the quadratic curve, that is, the gradient increases with the increase in energy. The effect of the rotational energy is small.



Intra dimer Intra row Inter row

Figure 4: The translation, rotation and vibration energy dependence of the scaled reaction probability

Figure 3: Main reaction path of the dissociative energy dependence of the scaled reaction probability

The results of true P_r are compared with those obtained by Jones et al. The variation in the P_r by the integration is about 10% even at maximum. The results of comparison for the translation energy ($T_r = T_v = 673\text{K}$) and substrate temperature (translation energy is set at 0.65 eV (5000K) and the other temperatures are set at 673K) dependences are shown in Figs. 5 and 6. The dependence of substrate temperature shows qualitative, but not quantitative, agreement with the experiments. However, the results obtained by other experiments for translation energy differ greatly from our results.

Discussion

The results presented in Fig. 5 show the discrepancies with the experiments, discussed below. According to Jones et al.[5], the vibration temperature of a translationally activated molecular beam is estimated at about 673K based on the nozzle temperature. However, these values were not measured directly. The result of changing the rotation and vibration temperature to 1173K is shown in Fig. 5. While P_r rises, the dependence of translation energy shows a similar tendency with a temperature of 673K. Therefore, we believe that this discrepancy is not caused by the increase in vibration temperature. Next, in order to detect the effect of reaction path, we calculated the translation energy dependence of P_r only through the intra-dimer site used for our fitting. P_r decreases by an order of magnitude, but shows the almost same tendency. Finally the following two issues are considered to be problematic in modeling. One is the difference in the calculation condition. The effects of roughness and corrugation need to be considered[5]. Calculation, which changes the incident angle and the condition of substrate, is considered to be necessary. The other is the difference in the potential energy surface. In general, if the reaction is greatly dependent on the translation energy, a potential barrier exists in the reactant path (early barrier); inversely, if the reaction is greatly dependent on the vibration energy, a potential barrier exists in the product path (late barrier)[13]. Since in our potential the energy barrier was lowered simply by raising the bond-order in the transition state, it might produce the energy surface of the late barrier. This result remains to be verified using a more accurate method such as the tight-binding method.

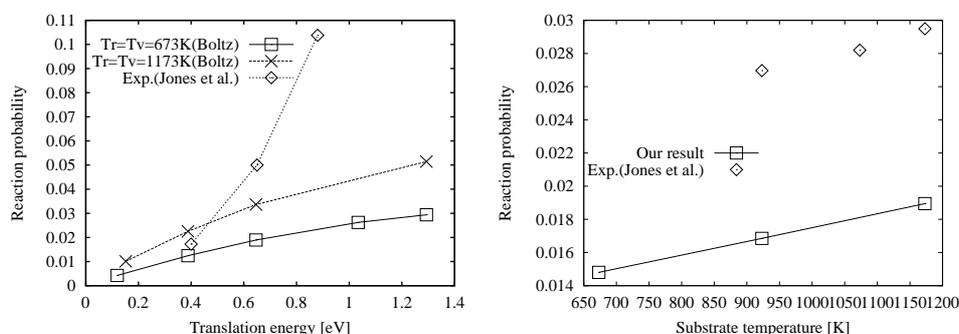


Figure 5: Translational energy dependence of the reaction probability. Figure 6: Substrate temperature dependence of the reaction probability.

Conclusion

We developed a new Si-H potential which reproduces the energy and vibration wave number of silicon clusters, the activation energies of hydrogen desorption from a Si(100) surface and silane dissociative adsorption. Using molecular dynamics with our potential, the dependence of the molecular and substrate temperatures on P_r of the transitionally activated process was investigated. The substrate temperature dependence agreed qualitatively with the experiment. The calculation showed linearity for translation energy dependence, while the experiment showed an exponential function. This is attributed to impact angle dependence and differences in the potential surface shape.

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