Full Simulation of Silicon Chemical Vapor Deposition Process

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Abstract. Chemical vapor deposition (CVD) process composes a complex system, where chemical reaction and heat and mass transfer interact with each other. And these macro-scale phenomena are deeply related to micro-scale mechanics. Hence multi-scale analysis is required to understand these complicated phenomena and to develop full-scale simulator of the CVD reactor. In this paper, we present the macro-scale simulation by the DSMC method. In those reactors, sometime the important species such as the reactive intermediates have extremely low density ratio. This causes the large statistical fluctuation in the DSMC method, where the number of particles and the calculation time are limited. We propose a new numerical method for this kind of problem and the whole process of silicon CVD is simulated by the new method. We simulate the following CVD process: the gas mixture of silane and hydrogen forms a free expansion jet through a nozzle orifice at the top of the reactor and interact with the heated substrate that is set vertical to flow, where silane decomposes into silylene and silane and silylene deposit onto the surface. It is confirmed that the new method is very effective and make it possible to analyze the CVD process more precisely.

1. INTRODUCTION

The importance of controlling and predicting thin film growth processes in the semiconductor industry goes on increasing, as the next generation devices require more increased component density and more decreased feature size. The diameter of silicon wafer is 200-300 mm and the thickness of thin film is a few nanometers in the present. But it is said that the film thickness becomes less than 1 nm in the near future. Chemical vapor deposition (CVD) process is generally used to deposit many kinds of such a film. Because CVD process is a complex system that involves chemical reaction and heat and mass transfer, the details of the phenomena in the reactor are not understood well in spite of the widespread commercial use. Therefore the reactors have been mainly designed empirically until now. However it can be done more efficiently and accurately using numerical method without having to rely on empirical data and it will save much time and cost to develop the new devices.

The studies about modeling of CVD process can be divided broadly into two groups. One is the study of the macro-scale analysis. This is about the whole flow filed in the reactor, that is, the spatial distribution of velocity, energy and density from the viewpoint of reactor size. These are evaluated by Navier-Stokes equations [1]-[3] or the DSMC method [4]-[6]. The other is the study of the micro-scale analysis and this contains intermolecular potential and collision dynamics from the viewpoint of molecular size [7][8]. In the actual CVD process these physical phenomena strongly interact each other and the multi-scale analysis must be needed as shown in Fig.1. In the CVD reactor, large amount of molecular collisions result in the deposition of thin film. And the molecular motion is controlled by nucleus or electron. But it needs enormous computational cost to solve the Shrödinger equations in order to obtain the whole flow filed in reactor. Then it is useful to extract the important element and to compose the inter-molecular potential. The same idea is also effective for composing the molecular collision model. Thus we can obtain the physical quantities without empirical data. Therefore our aim is to couple the different kind of scales and develop the full-scale model to predict the accurate performance of the CVD reactor. The work reported here describes macro-scale analysis of low-pressure neutral CVD process using the DSMC method.

The deposition of polycrystalline silicon from silane is one of the most studied CVD process and a large number of studies have been made by the DSMC method over the last decade or so. Despite many studies most of them are limited to the qualitative ones because the key gas-phase reactions and the surface reaction occur infrequently and the large differences of number density between species cause statistical problem and need enormous computational

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14. ABSTRACT
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cost. In the process of polycrystalline silicon, the density ratio of silylene to silane is much smaller than unity in some condition. But the reactive sticking coefficient of silylene is much larger than that of silane and the difference of density is offset. As to the contribution to the deposition, therefore both of them should be modeled accurately. In this paper we introduce a new DSMC schemes for the trace species chemistry using particle dependent weight factors in order to overcome this difficulty. First, the new method is described and the differences between the new method and the conventional one are discussed. Next, low-pressure silicon CVD process is modeled by this new method and the effect is evaluated.

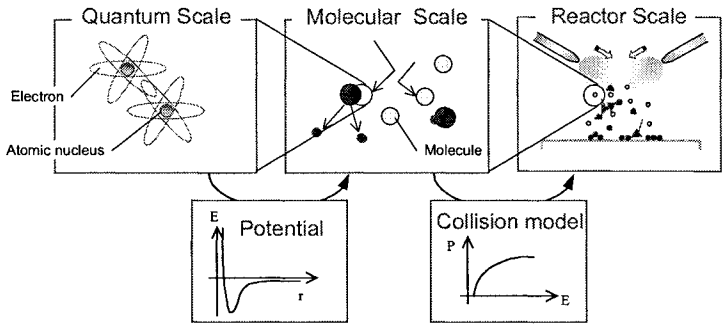

FIGURE 1. Schematic diagram of the multi-scale analysis

2 GAS-PHASE REACTION WITH WEIGHT FACTOR

First, let us suppose a typical irreversible dissociation reaction as

$$\mathrm{AB+M} \rightarrow \mathrm{A+B+M}. \tag{1}$$

Here, AB represents the dissociating molecule, A and B are atoms or molecules, and M is the third body atom or molecule. A basic chemistry model in DSMC method is the total collision energy (TCE) model proposed by Bird [9]. In this model, the total energy E_c is compared with activation energy E_a. When E_c is greater than E_a, the probability of reaction P_r is calculated. The probability P_r is obtained by integrating the known equilibrium distribution $f(E_c)$ for all the total collision energy and equating it to a chemical rate constant $k(T)$ at temperature T as

$$k(T) = \int_{E_a}^{\infty} \sigma_t g P_r f(E_C) dE_C = AT^{\eta} exp(-E_a/kT), \tag{2}$$

where σ_t is the collision cross section, g is the relative velocity, E_a is the activation energy of the reaction, A and η are constants, and k is the Boltzmann constant. As mentioned above, when the reaction is infrequent, that is, probability P_r is low, it causes the large difference of density between the chemical species. Hence the species dependent weight factor W_i (i=AB, A, B, M) is usually applied to evade the statistical problem. In the following discussion, we suppose that species AB is diluted gas and species M is carrier gas and that $W_M > W_{AB} > W_A = W_B$. Let us start with the calculation of the probability P_r in the following section.

2.1. Conventional Method

In the TCE model probability P_r is assumed to have the form

$$P_r = C_1 \left(1 - \frac{E_a}{E_c}\right)^{\eta+\zeta_{ij}+1/2} E_c^{\eta+\omega_{ij}-1}, \tag{3}$$

where C_1 is constant, which is determined from Eq. (1) and ζ_{ij} is the average number of internal degree of freedom, which is arbitrary parameter in this model and ω_{ij} is the viscosity-temperature exponent. In the conventional method, probability P_r is determined by Eq. (3) every time the collision with $E_c > E_a$ occur and compared with the random

number to decide if the collision is reactive or not. If the collision is reactive, the reactant AB vanishes from the computational region and the products A and B are created. However, this method has severe problem when the ratio of weight factor of species A and B to species AB is far from unity. For example, when $W_{AB}=1.0\times10^4$ and $W_A=W_B=1.0$, the 10,000 computational particles of species A and B are created in the same position and at the same time. As a result, tens of thousands of computational particles or enormous computational time must be needed to collect the statistic. The engineering DSMC simulations cannot afford to accept such a requirement.

2.2. New Method

We propose the new method to deal with the trace species chemistry much more efficiently. The basic idea of the new method is gradual decrease of the reactants weight every reactive collision, and this method consists of three steps. In the first step, the expected value that one computational particle is involved in the reaction is evaluated and the computational particle is divided into two parts. In the next step, chemical reaction occurs in one part and another part is regarded as elastic or inelastic collision with the conventional method by Bird [9]. The last step is to merge the two parts if there is some remainder of reactant after reactive collision.

2.2.1. Step 1

Again we consider the chemical reaction expressed in Eq. (1). The first step is to divide the computational particle of AB and M into two parts. If we suppose that a computational particle AB is a set of W_r virtual particles, where $W_r=W_{AB}/W_A$, the number of virtual particles involved in chemical reaction is expected from Eq. (3) as,

$$\langle W_r \rangle = W_{AB}/W_A P_r = W_r C_1 \left(1-\frac{E_a}{E_c}\right)^{\eta+\zeta_{ij}+1/2} E_c^{\eta+\omega_{ij}-1}. \tag{4}$$

This means that $<W_r>$ virtual particles out of W_r are involved in reaction. From this discussion the computational particle of AB and M are divided into the virtual two particles as shown in the left side of Fig.2. One is the part that is involved in chemical reaction with the weight factor expressed as Eq. (5). And the collision of another part is regarded as elastic or inelastic and the weight factor is expressed as Eq. (6).

$$W_{AB}^r = W_M^r = \langle W_r \rangle \tag{5}$$

$$W_{AB}^n = W_{AB} - \langle W_r \rangle, \quad W_M^n = W_M - \langle W_r \rangle \tag{6}$$

Though the computational particles are divided, the mass conservation is still satisfied.

2.2.2. Step 2

In this step, collisions are performed using the conventional DSMC method for both parts as shown in Fig.2. First, we consider the reactive collision part. As mentioned above, virtual particles AB^r and M^r have the same weight. Hence the conventional TCE model can be applied, and species A and B are created with the weight factor W_A and W_B. The number of the created computational particles of A and B is W^r_{AB}. Though the virtual particle AB^r vanishes, the virtual particle M^r still remains with the weight of W^r_M. Next, nonreactive collisions for another part are considered. Because the weights of the virtual particles AB^n and M^n are not the same, the linear momentum and energy conservation are not satisfied with the conservative method. The conservative weighting scheme by Boyd [11] gives good solution to this problem. This scheme conserves both linear momentum and energy during collisions. Therefore all the post-collision and post-reaction velocity and energy are determined. Though all the products A and B are created without consuming the reactants AB, the mass conservation is hold by decreasing the weight of AB

2.2.3. Step 3

The last step is to determine the velocity and energy of third body M as shown in Fig.2. Two virtual particles M^r and M^n have the velocity vector $\boldsymbol{C}^r_M$ and $\boldsymbol{C}^n_M$, and have the different weight W^r_M, W^n_M respectively. Again the

conservative weighting scheme by Boyd can be applied to merge together the two virtual particles. The final velocity vector C'_M is evaluated as

$$C_M = (1-\phi)C_M^n + \phi C_M^r \tag{7}$$

where $\phi = \langle W_r \rangle / W_M$. And the energy loss between the pre- and post-collision state is written as

$$\Delta E = \sum_i m_M \phi(1-\phi) C_i^n C_i^r \,. \tag{8}$$

This energy loss is added by the same way as Boyd's method. And the internal energy is also determined similarly. This step can be omitted if the reaction does not involve the third body like the exchange reaction.

It is noted that each computational particle of products A and B will be created each time step with the appropriate weights and that the exact conservation of momentum and energy is satisfied at each collision by this new method. Although the basic concept of this method is the same as the integral detailed balancing concept by Bartel [10], this method is based on the collision dynamics and broadly applicable.

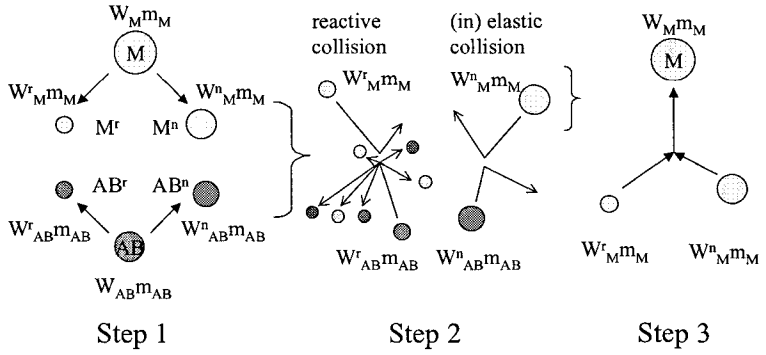

FIGURE 2. Schematic diagram of the new trace chemistry method

2.3. Application Results

We have compared the new method with the conventional one by calculating the reaction rate constant of Eq. (1). The test calculation is performed in thermal equilibrium single cell at temperature range from 1000K to 1500K. The initial component of gas mixture consist of is AB (1%) and species M (99%), and the weight factor is W_{AB}:W_M=1:99. Initially each number of computational particles is 10,000 respectively. The number of species AB gradually decreases and the products A and B are created every time step. The reaction rate constant is given by Eq.(2), where the values are set to A=1.5×10^{-14}, η=0, E_a=3.0×10^{-19}. Each calculation has been continued until the calculated reaction rate reaches almost constant. The left figure of Fig.3 shows that a good agreement with theory is obtained for both methods. It is clear that the new method can reproduce the molecular collision correctly. And in the right of Fig.3, the new method gives the results much faster than the conventional method. In the very low reaction probability at 1000K the calculation efficiency increases by a factor of 100.

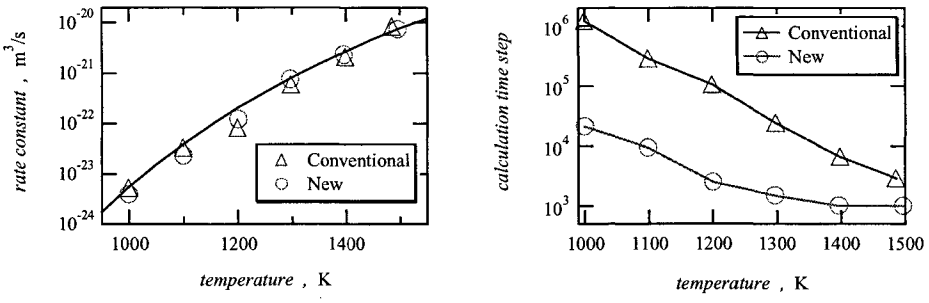

FIGURE 3. Calculation of the chemical rate constant and the velocity distribution

3. SURFACE REACTION WITH WIGHT FACTOR

Let us consider the case that the molecules adsorb to the surface with the reactive probability γ. If γ is much smaller than unity, enormous computational time must be needed until the certain numbers of molecules adsorb. And when the weight factor is used to evade that problem, the statistical problem still remains like the gas-phase reaction, that is, the enormous number of species absorb at the same point and the same time. But the new method can be the solution to this kind of problem. Consider the case that a computational species A with weight W_A adsorb to the surface with the probability γ. If we assume that a computational particle A is a set of W_A virtual particles, the number of virtual particles that adsorb to surface every time the particle A reach the surface is expected as,

$$\langle W_A \rangle = W_A \gamma . \tag{9}$$

Then the computational particle A is divided into two part again. That is, one part is adsorbed to the surface with weight $<W_A>$, and another escapes from the surface with weight W_A-$<W_A>$. Thus with the appropriate weight virtual particles will adsorb each time step and decreasing the weight of computational particle A satisfies the exact mass conservation.

We have compared this method with the conventional one by calculating the distribution of the number of molecules that adsorb to the surface. The test calculation is performed in the single cell with the wall at one side of the boundary. When a particle reaches to the wall, the probability γ is compared with the random number to decide if the particle adsorb or not. If it is not reactive impact, the diffusion reflection is applied. The initial number of computational particles is 100,000 and the calculation has been continued until the 0.1 % of molecules adsorb to the wall. As shown in the left side of Fig.4, it is clear that the new method gives the flat distribution while the meaningless result is only obtained by the conventional method in this calculation time. Fig.5 shows the required calculation time to obtain the flat distribution, and the new method gives the excellent efficiency even if the very low γ, and the calculation time is reduced by a factor of 10,000.

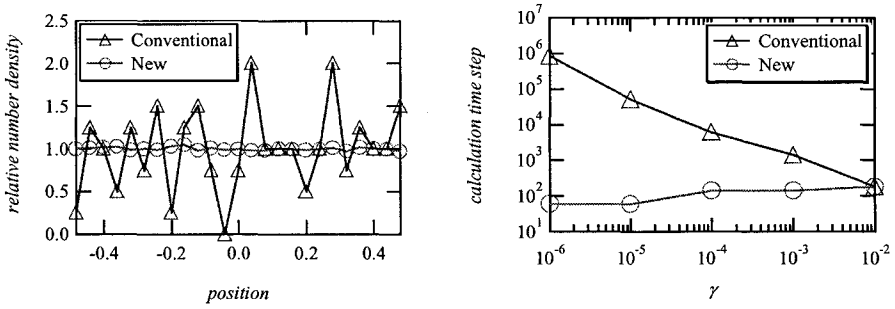

FIGURE 4. Comparison of uniformity and calculation time as to surface reaction

4 APPLICATION TO SILICON CVD PROCESS

4.1. Flow Condition and DSMC Method

Using the new method as mentioned above, CVD process is modeled by the DSMC method. As shown in Fig 5 the axisymmetric vertical CVD reactor with cold walls with temperature T_w is considered. The heated substrate with temperature T_s is set to vertical to flow at *5d* below from the *r*-axis and the diameter of substrate is d_s. The mixture of reactant gas silane and carrier gas hydrogen expands through an orifice of diameter d_n and forms a free expansion jet. The density ratio of silane to hydrogen at inlet is 1:99 and the upstream and downstream pressure is 1 Torr and 10 mTorr, respectively. The three chemical reactions in the gas-phase and at substrate are considered as

$$SiH_4(g) + H_2(g) \rightarrow SiH_2(g) + 2H_2(g), \tag{10}$$

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g), \tag{11}$$

$$SiH_2(g) \rightarrow Si(s) + H_2(g), \tag{12}$$

where (g) and (s) mean gas and solid respectively. In the gas phase silane decomposes into silylene by the collision with hydrogen only. We use the kinetic constants of the Arrhenius relation by Coltrin [1] and A=1.64×10^{-14}m^3/s, η=0, E_a=3.337×10^{-19}J in Eq.(2). At substrate species react according to the Eq.(11) and (12) and in accordance with Moffat and Jensen [12], we assume the reaction probability γ as

$$\gamma_{SiH2} = 1.0, \quad \gamma_{SiH4} = A_s \exp(-E_s / kT_s) \tag{13}$$

where A_s=5.37×10^{-2}, E_s=1.298×10^{-19}J. The silicon atom is adsorbed at the impact points and the hydrogen molecules are desorbed with Maxwell velocity distribution at the substrate temperature. The computational domain includes the half cross section of the axisymmetric reactor in (r, z) coordinate system. Specular reflection is supposed for all the computational particles which across the symmetric axis. And vacuum condition is supposed at the gap between the substrate and the reactor wall, and no computational particle enters from the gap. The computational domain consists of about 1.0×10^4 grid cell and the total number of computational particles is about 5.0×10^5. The total execution time is on Alpha PC.

The DSMC calculation follows the basic statement of the Bird's method [9] except the chemical reaction. Collisions of computational particles are simulated using hard sphere model because the lack of the reliable data of Si-H system for other model like variable hard sphere model. And the null collision method [13] is used in evaluation of the collision number. The Borgnakke-Larsen statistical model [14] evaluates energy exchange between translational and other internal modes. For the chemical reaction, the new and conventional methods are applied. In the new method, the weight of every computational particle can be different and the maximum collision number must be evaluated considering the difference of weight. When the two computational particles A_i and B_i that are different kind of species collide, the maximum number of collision M_{max} is estimated as

$$M_{max} = \frac{1}{2} max\{\langle W_{A,i}\rangle, \langle W_{B,i}\rangle\} N_A N_B (g\sigma)_{max} \Delta t V^{-1}, \tag{14}$$

where $<W_{A,i}>$ means the expected value of weight of the particles A in the grid cell, $max\{A,B\}$ means the maximum value of the two, N_A is the number of the computational particles A in the grid cell, g is the relative velocity, σ is the collision cross section, Δt is the time step, and V is the volume of the grid cell. For the collisions of the same kind of species, N_B can be replaced to (N_A-1).

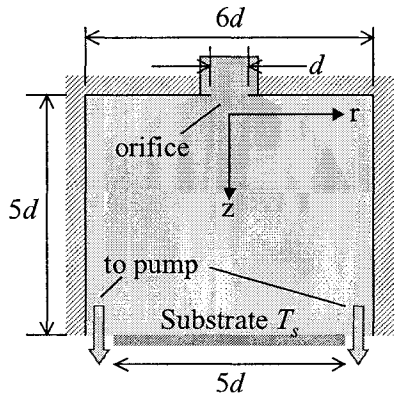

FIGURE 5. Reactor geometry and computational domain

4.2. Results and Discussion

We show one example of the calculation of CVD process. In this calculation, the temperature of substrate is 1500K and the inlet pressure is 1 Torr. Fig.6 indicates the distribution of number density and the averaged translational temperature. A free expansion jet is formed and the high temperature area is appeared at heated surface. It is supposed that the dissociation reaction can occur in this area. And as the right figure indicates, silane is

accelerated by lighter hydrogen and large temperature jump at the substrate is present. Also in the area of high energy silane, the dissociation is expected. We can obtain the same result about the flow properties by the new and conventional method. But, the gas-phase reaction does not occur by the conventional method because of the reason mentioned above. And only by the new method we can reproduce the dissociation of silane. Fig.7 indicates the distribution of number density of silylene. We can see the high-density area at the sidewall against our expectation. This does not mean that the reaction occur near the cold sidewall. As shown in the vector plot of velocity in Fig.7, the most likely explanation is that the produced silylene is brought to sidewall by the convection. And the diffuse reflection of the sidewall causes the high density of silylene. But it is doubtful whether the very reactive radical of silylene does not adsorb the cold wall at 300K. It is the future work to inquire this in detail. Next, let us discuss about the deposition distribution at substrate. As shown in Fig.8, the distribution of the deposits from silane is extremely uniformity. On the other hand, the reaction probability of silylene is much higher and the distribution reflects the number density in the gas-phase. The rough distribution of deposits from silylene comes from the statistical fluctuation and it is not derived from the physical phenomena. The optimization of calculation condition must be done. In this calculation condition the contribution ratio of silylene to silane is about 0.1 and it is very small compared with the atmospheric reactor. This can be explained by the small amount of the collisions due to the low pressure.

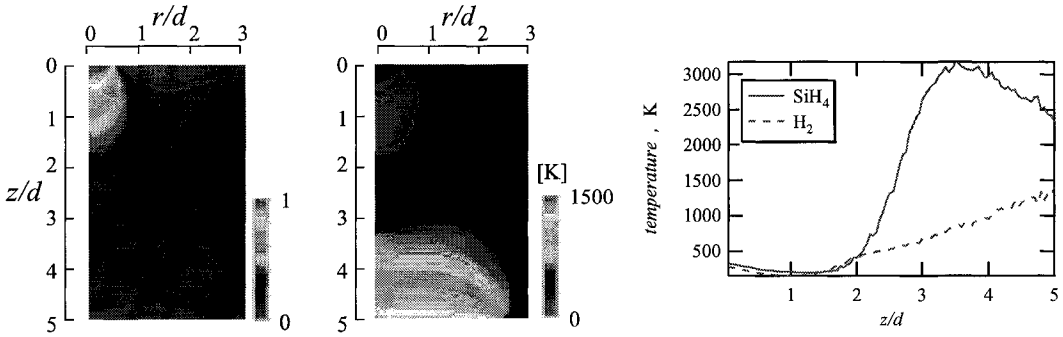

FIGURE 6. Distribution of the number density, temperature

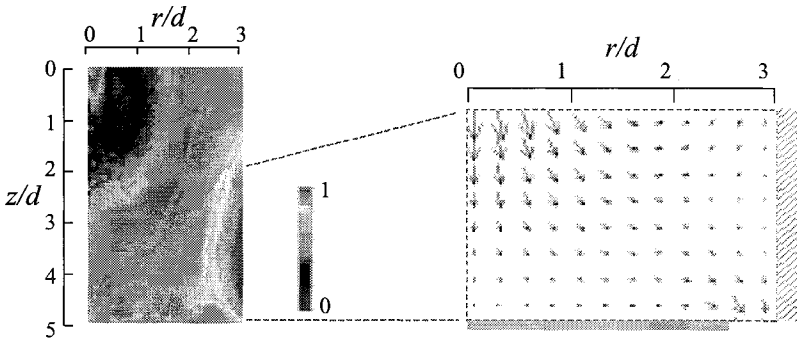

FIGURE 7. Density distribution of silylene

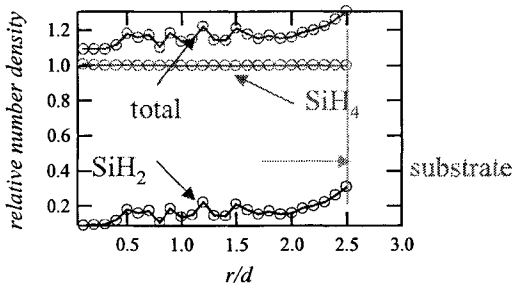

FIGURE 8. Deposition at heated substrate

5 CONCLUSION

We have introduced the new trace chemistry method and applied to the silicon CVD process. The new method was applied to both the gas-phase and the surface reaction and it is very effective. By this method the enormous computational cost can be reduced. In the analysis of CVD reactor we succeed to reproduce the formation of silylene in the gas-phase. The optimization of the calculation condition and the further examination of boundary condition must be done. And in order to develop the full-scale model, micro-scale analysis including quantum effect must be considered. These are the perspective for the near future.

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