Motion of nanoparticles in rarefied gas flows

K. Nanbu* and T. Otsuka*

*Institute of Fluid Science, Tohoku University, Sendai 980-8577, Japan

Abstract. Solar cells have been made from hydrogenated amorphous silicon (a-Si:H) films. The films including Si nanoparticles by 3% in the volume fraction have been found to possess good properties. In order to find the method to control this volume fraction, the motion of Si nanoparticles in the rarefied flow of H_2 and SiH_4 is examined for a CVD (chemical vapor deposition) reactor by use of the DSMC method.

INTRODUCTION

If every house in the world had a wide solar cell on its roof, a large reduction of CO_2 around the globe would surely be realized. Solar cells are made from hydrogenated amorphous silicon (a-Si:H) films or microcrystalline films. Recently, a better alternative is proposed by the group of Kyushu University [1]. It is the a-Si:H films into which nanocrystalline particles of silicon are dispersed. This film has the light absorption coefficient as large as the usual a-Si:H. Moreover, it shows a small light-induced degradation and a good carrier transport properties as in the case of the microcrystalline films.

In order to realize the optimum property for such nanoparticle-dispersed films, the transport of Si nanoparticle to the surface of deposited a-Si:H films must be controlled in such a way that the volume fraction of Si nanoparticles dispersed into the film is 3%. To find a method to control the volume fraction, the motion of the nanoparticles in rarefied gas flows of H_2 and SiH_4 is examined for a CVD (chemical vapor deposition) reactor using the DSMC simulation.

MODELING OF PHENOMENA

Figure 1 shows the CVD reactor treated here. There are two electrodes in the cylindrical chamber with diameter d_3 and height h_3. The diameter and height are d_1 and h_1 for the upper electrode, and d_2 and $h_3 - h_2$ for the lower electrode. The upper electrode is powered by a radio frequency source and the lower is grounded. Source gases H_2 and SiH_4 are fed uniformly from the shower head set on the lower surface of the upper electrode. Nanoparticles of silicon, $(Si)_n$, are generated by the electric discharge between the two electrodes; SiH_4 molecules are dissociated by electron impact and released Si atoms grow into a nanoparticle by repetition of collisions with other Si atoms. Gases and nanoparticles are pumped out from the annular exist at $z = h_3$.

The mechanism of the generation and growth of a nanoparticle is complicated. Replacing the mechanism by a very simple model, we examined the flows of H_2, SiH_4, and $(Si)_n$ in the reactor of Fig. 1. There is a great difference of molecular mass between the carrier gas and nanoparticle. Our concern is the velocity slip among H_2, SiH_4, and $(Si)_n$.

OUTLINE OF SIMULATION

Gas is a mixture of H_2, SiH_4, and $(Si)_n$. Rarefied flows of the gas mixture are calculated using the DSMC. A three-dimensional cell network is introduced for a general use. The cell sizes are Δr and Δz in the r- and z- direction, respectively. They are constant. The cell boundary (grid point) is given by $r_i = i\Delta r$ and $z_j = j\Delta z$. The region between r_{i-1} and r_i has the area $(2i-1)\pi(\Delta r)^2$. The region is divided into $K[= 2(2i-1)]$ subregions in the θ- direction. The cell boundary is $\theta_k = k\Delta\theta$, where $k = 1, 2, \cdots, K$ and $\Delta\theta = 2\pi/K$. The cell volume V_c is $\pi(\Delta r)^2\Delta z/2$ for any cell. Free motion and collision of simulated molecules are treated separately in the DSMC.

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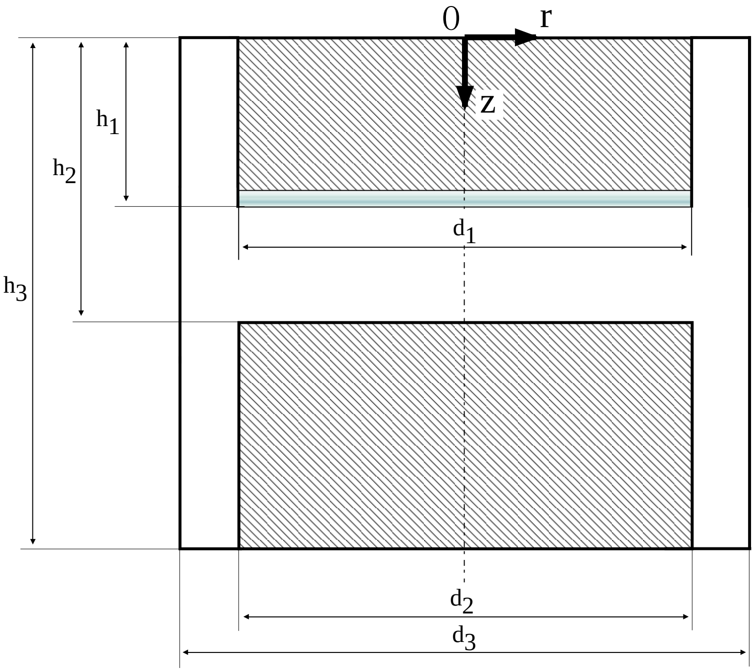


FIGURE 1. Model of CVD reactor

FREE MOTION

Let 1, 2, and 3 denote the species H_2, SiH_4, and $(Si)_n$, respectively. Since there is a large difference among the number densities of three species, we introduce weight W_s for a simulated particle of species s, where s = 1, 2, or 3. Let Q_1 and Q_2 be the mass flow rates of H_2 and SiH_4 in units of sccm. These gases are fed from the shower head. Since H_2 is a carrier gas, usually $Q_1 \gg Q_2$. We choose W_2 from $W_2/W_1 = Q_2/Q_1$. The weight W_1 is determined from $W_1 = n_0V_c/N_0$, where n_0 is the number density of H_2 and N_0 is the number of simulated particles in a cell at time zero. The number of incoming molecules in Δt is

$$F_i = \frac{n_{\mathrm{STP}}Q_i\Delta t}{60 \times 10^6 W_i}$$

where n_{STP} is the standard number density at 273 K and 1 atm. Our choice of W_i yields $F_1 = F_2$.

The nanoparticle $(Si)_n$ is assumed to be produced by the reaction.

$$n\mathrm{SiH}_4 \to (\mathrm{Si})_n + 2n\mathrm{H}_2 \tag{1}$$

Let m_0 and m_3 be the mass of Si and $(Si)_n$. We see that the number of SiH_4 molecules in producing one $(Si)_n$ is m_3/m_0. The mass flow rate of SiH_4 is Q_2. A part of Q_2 is consumed for reaction (1) and the rest of Q_2 is pumped out from the exit. Let ηQ_2, where $0 < \eta < 1$, be consumed in the reaction. Therefore,

$$Q_3 = \frac{\eta Q_2}{m_3/m_0} \tag{2}$$

is the rate of production of $(Si)_n$. It is assumed that $(Si)_n$ is produced spatially uniformly in the region between the electrodes. We choose W_3 as $W_3/W_2 = m_0/m_3$. If $\eta = 1$ in eq.(2), this means that $W_3/W_2 = Q_3/Q_2$.

The shower head has many tiny holes. The flow of the mixture of H_2 and SiH_4 is regarded as sonic at the exit of the hole. That is, the flow velocity V^* and temperature T^* are given by [2]

$$V^* = \sqrt{\gamma R T^*}$$

$$T^* = \frac{2}{\gamma + 1} T_0$$

where, γ is the specific heat ratio for the mixture, T_0 is the stagnation temperature that is close to the room temperature, $R = k/m$, k is the Boltzmann constant, and m is the molecular mass of the mixture. The velocities of incoming molecules are sampled from the Maxwellian distribution with the flow velocity V^*. The gas pressure between the two electrodes is set to a given value by adjusting the transmission probability of a particle at the annular exit. The diffuse reflection model is used on any solid wall.

MOLECULAR COLLISION

As before, let 1, 2, and 3 denote H_2, SiH_4, and $(Si)_n$. There are six types of collision. Like collisions are 1-1, 2-2, and 3-3, and unlike collisions are 1-2, 1-3, and 2-3. The rigid sphere model is used for three species. Let σ_s be the molecular diameter. We set $\sigma_1 = 0.2745$ nm and $\sigma_2 = 0.4187$ nm, where the diameter of CH_4 is used instead of the diameter of SiH_4 [3]. The diameter d_n of nanoparticles is $0.5-5$ nm [1]. Here d_n is the input data. The mass m_3 of a nanoparticle is chosen as

$$m_3 = \frac{4}{3}\pi\left(\frac{d_\mathrm{n}}{2}\right)^3\rho$$

where $\rho(= 2.33\times10^3\mathrm{kg/m^3})$ is the density of solid silicon in bulk. We have $m_3/m_2 = 22.90$ for $d_\mathrm{n} = 1$ nm. The collisions in each cell are treated using the maximum collision number method [4]. Let $N_{sr}^{(\max)}$ be the maximum collision number between species s and r. It is

$$N_{sr}^{(\max)} = C_{sr}\frac{(N_s-\delta_{sr})N_r}{V_\mathrm{c}} \tag{3}$$

where

$$C_{sr} = \frac{1}{1+\delta_{sr}}\max(W_s,W_r)g_{sr}^{(\max)}\sigma_{sr}\Delta t \tag{4}$$

where δ_{sr} is the Kronecher delta, N_s is the number of simulated molecules of species s in a cell, the diameter σ_{sr} is defined by $\pi(d_s+d_r)^2/4$, and $g_{sr}^{(\max)}$ is the maximum value of the relative speed between two molecules in species s and r. It is estimated as $g_{sr}^{(\max)} = 2.5\sqrt{kT_\mathrm{ref}/\mu_{sr}}$, where $\mu_{sr} = m_s m_r/(m_s+m_r)$, and T_ref is a reference temperature. The procedure to calculate s-r collisions in a cell is as follows [4]. Repeat the following steps (i)$-$(ii) $N_{sr}^{(\max)}$ times.

(i) Sample two particles randomly, one from species s and another from species r. Let $(\mathbf{c}_s, \mathbf{c}_r)$ be the velocities of this pair. Calculate $g_{sr} = |\mathbf{c}_s - \mathbf{c}_r|$. If $U < g_{sr}/g_{sr}^{(\max)}$, go to (ii), and if not, go to the next do-loop of $N_{sr}^{(\max)}$. Here U is a uniform random number of $0 < U < 1$.

(ii) Replace $\mathbf{c}_s$ by $\mathbf{c}_s'$ with probability $W_r/\max(W_s,W_r)$ and $\mathbf{c}_r$ by $\mathbf{c}_r'$ with probability $W_s/\max(W_s,W_r)$, where $(\mathbf{c}_s', \mathbf{c}_r')$ are the post-collision velocities given by

$$\mathbf{c}_s' = \mathbf{W} + \frac{m_r}{M}g_{sr}\mathbf{R}$$

$$\mathbf{c}_r' = \mathbf{W} - \frac{m_s}{M}g_{sr}\mathbf{R}$$

where $M = m_s + m_r$, $\mathbf{W} = (m_s\mathbf{c}_s + m_r\mathbf{c}_r)/M$, and $\mathbf{R}$ is a unit vector with a random direction.

RESULT AND DISCUSSION

Computational conditions are as follows. The gas pressure p of H_2, which is close to the total pressure, is $10-20$ Pa, the mass flow rate Q_1 is $500-1000$ sccm, $Q_2 = Q_1/500$, and the diameter d_n of nanoparticle is $0.5-2$ nm. The geometry of the CVD reactor is $d_1 = d_2 = 80$ mm, $d_3 = 100$ mm, $h_1 = 30$ mm, $h_2 = 50$ mm, and $h_3 = 90$ mm.

First we show the flow fields of H_2, SiH_4, and $(Si)_n$ for Q_1 = 500 sccm, Q_2 = 1 sccm, p = 20 Pa, and d_n = 1 nm. Figures 2, 3, and 4 show the flow velocities of three species. The flow of SiH_4 is similar to that of H_2. Two vortices exist near the corners of the upper and lower electrodes. Nanoparticles flow slowly. The flow of $(Si)_n$ near the edge of the electrode is similar of that of the carrier gas H_2 but the lower vortex does not appear for $(Si)_n$. The flow of $(Si)_n$ near the exit is very slow, almost retarded. Figures 5, 6, and 7 show the number densities of H_2, SiH_4, and $(Si)_n$. As for H_2, the density decreases in the downstream region. But for SiH_4 and $(Si)_n$ the opposite is true. Figures 8, 9, and 10

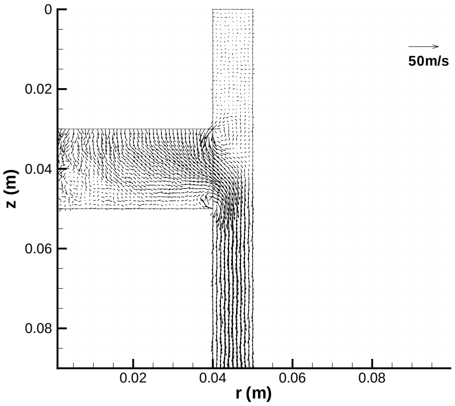


FIGURE 2. Velocity of H_2

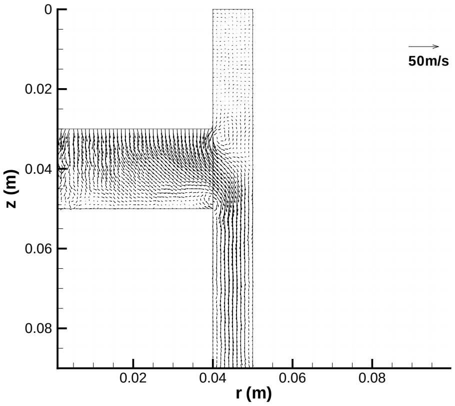


FIGURE 3. Velocity of SiH_4

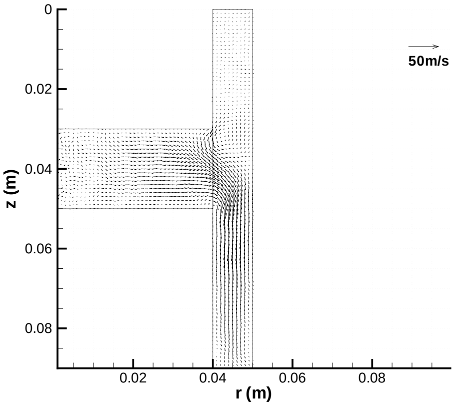


FIGURE 4. Velocity of nanoparticle (d_n = 1.0 nm)

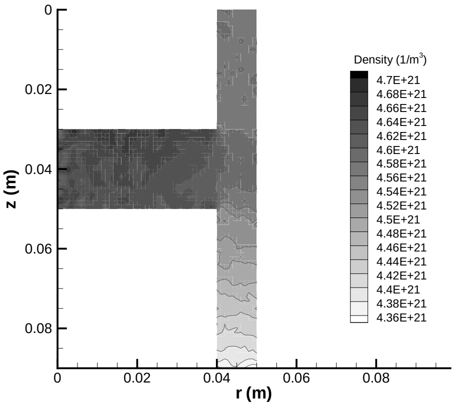


FIGURE 5. Density of H_2

show the effect of the size d_n on the flow velocity of nanoparticles. The lower vortex found for d_n = 0.5 nm disappears for d_n = 2 nm. Figures 11, 12, and 13 show the number densities for d_n = 0.5, 1.0, and 2.0 nm. For all three cases the density is highest near the exit. The density gradient along the streamline from the shower head to the exit increases with the size of nanoparticle. We examined the effect of pressure on the velocity and density fields of nanoparticles by comparing the data for p = 10 Pa and 20 Pa. We have seen that the effect is small. Also, we examined the effect of the mass flow rate on the flow field of nanoparticles, by comparing the data for Q_1 = 500 and 1000 sccm. The pressure is 20 Pa and the size d_n is 1 nm. Although the velocity is higher for 1000 sccm, the effect on the density field is small. In order to fabricate nanoparticle-dispersed films with the best quality, control of the flux of nanoparticles onto the lower electrode is important. Figure 14 shows the flux for Q_1 = 500 sccm, Q_2 = 1 sccm, and p = 20 Pa. We see that the flux is uniform on the electrode in particular for d_n = 0.5 and 1.0 nm. This means the correctness of the choice of the present operating condition. The flux is approximately proportional to d_n^{-4}. The effect of Q_1 on the flux is examined for p = 20 Pa and d_n = 1 nm. The effect is small; The flux for Q_1 = 1000 sccm is larger by 10% than the flux for Q_1 = 500 sccm. Figure 15 shows the effect of pressure p on the flux. When p is halved from 20 Pa to 10 Pa, the flux is also halved; The flux is proportional to p.

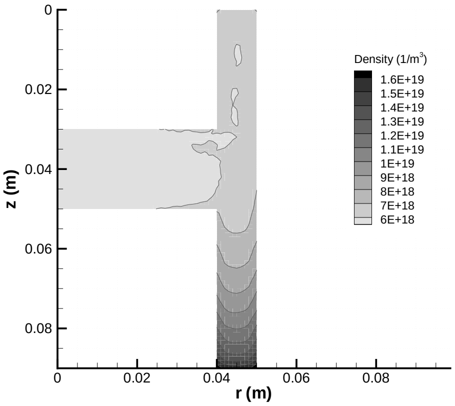


FIGURE 6. Density of SiH_4

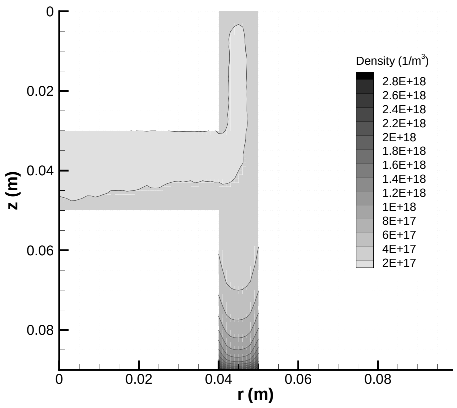


FIGURE 7. Density of nanoparticle (d_n = 1.0 nm)

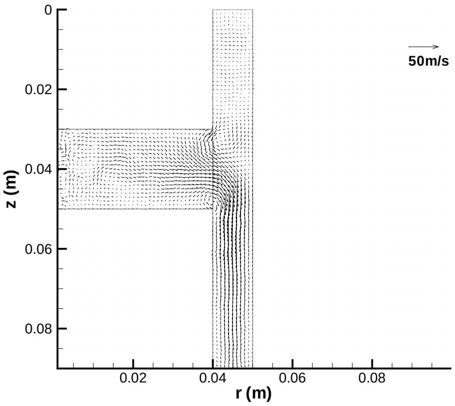


FIGURE 8. Velocity of nanoparticle (d_n = 0.5 nm)

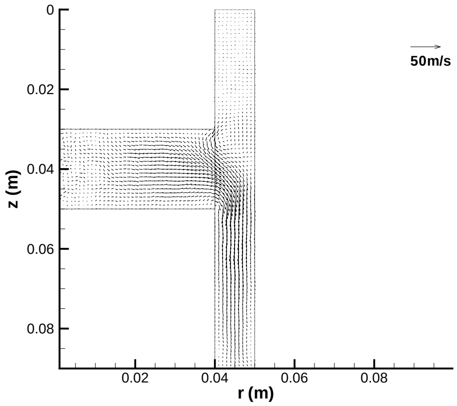


FIGURE 9. Velocity of nanoparticle (d_n = 1.0 nm)

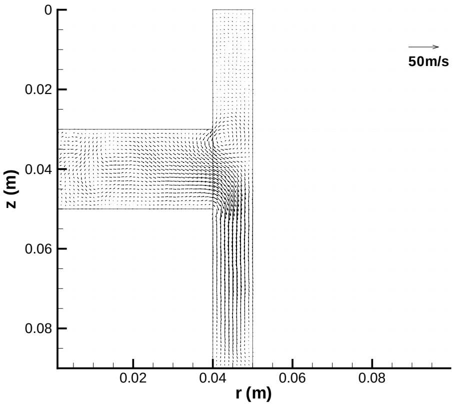


FIGURE 10. Velocity of nanoparticle (d_n = 2.0 nm)

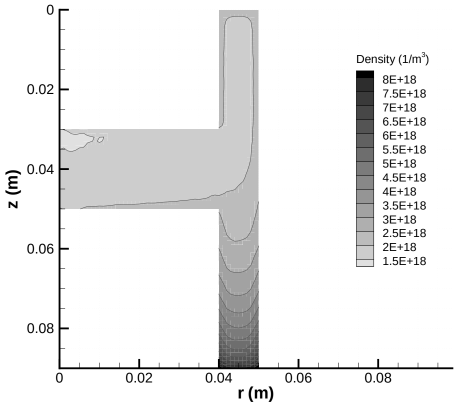
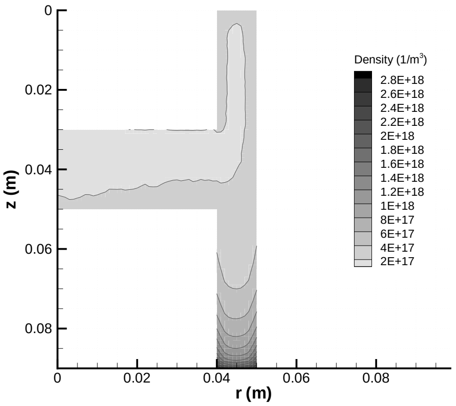


FIGURE 11. Density of nanoparticle (d_n = 0.5 nm)



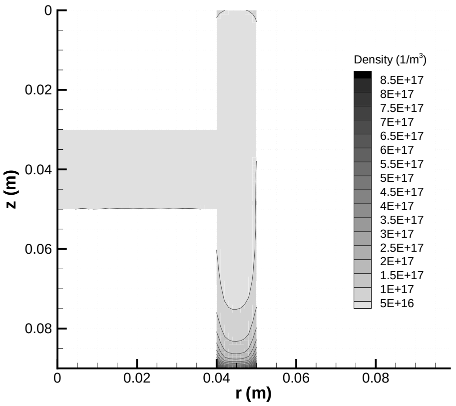
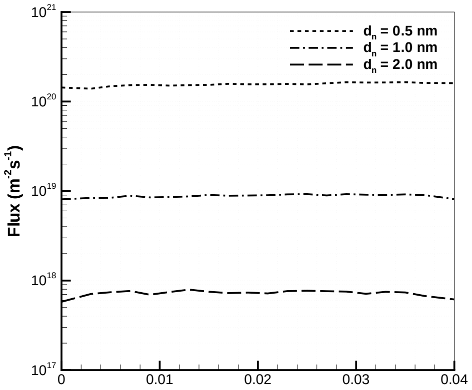


FIGURE 12. Density of nanoparticle (d_n = 1.0 nm) **FIGURE 13.** Density of nanoparticle (d_n = 2.0 nm)



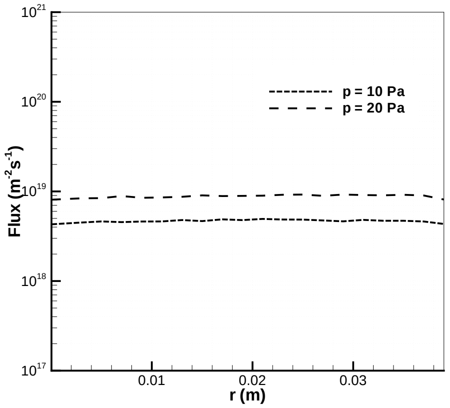


FIGURE 14. Flux of nanoparticles **FIGURE 15.** Flux of nanoparticles

CONCLUSIONS

Flow field of silicon nanoparticles in the rarefied flow of H_2 and SiH_4 is examined using the DSMC. The pressure p is $10-20$ Pa, the mass flow rate Q_1 of H_2 is $500-1000$ sccm, and the size d_n of nanoparticle is $0.5-2.0$ nm. We conclude as follows.

1. The flux of nanoparticles onto the wafer is nearly proportional to d_n^{-4}.
2. The flux is almost independent of Q_1.
3. The flux is nearly proportional to p.

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