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Citation	Nanoscale and Microscale Thermophysical Engineering. 2013, 17(1), p. 1-9
Version Type	AM
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A Molecular Dynamics Study on Wetting Phenomena at a Solid Surface with a Nanometer-Scale Slit Pore

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A Molecular Dynamics Study on Wetting Phenomena at a Solid Surface with a Nanometer-Scale Slit Pore

Molecular dynamics simulations were conducted for the liquid wetting phenomena on a solid surface with a nanometer-scale slit pore using the Lennard-Jones potential. The objective was to investigate qualitatively how the width of the slit pore and the liquid-solid interactions influence the dynamic phenomena of the liquid molecules. The results show that the intensity of the liquid molecule–solid atom interaction will determine whether or not the wetting phenomenon occurs (that is, whether the inside of the slit pore will be filled with liquid molecules within a definite period of time), and the characteristic time of the wetting phenomenon.

Keywords: molecular dynamics, wetting phenomena

Introduction

In semiconductor manufacturing, wafer cleaning processes account for a large part of the total manufacturing process, and are considered to be key to the improvement of final device performance. Recently, new materials such as copper and low-k dielectrics have been introduced to semiconductor devices, the features of which are shrinking to the nanometer scale [1]. Under the influence of those trends, stricter standards are required for wafer cleaning processes. In order to deal with this situation, the understanding of nanometer-scale phenomena is becoming more important in the semiconductor device manufacturing process. This is especially true for the wet cleaning process, where a nanoscale approach is expected to elucidate more fundamental cleaning mechanisms to solve complex problems which occur in the wet process [1,2]. However, the wet cleaning process involves nanoscale phenomena at the liquid-solid interface, and the cleaning mechanism has been considered to be difficult to clarify from the continuum mechanics point of view.

On the other hand, some molecular dynamics simulations have been conducted for phenomena related to the liquid-solid interface, and a variety of results and discussions have been published [3-7]. Those results show that the liquid-solid interaction greatly influences phenomena at the liquid-solid interface, and demonstrate the validity of molecular dynamics simulations to understand wetting phenomena at the nanometer scale.

In the present study, molecular dynamics simulations were conducted to examine liquid wetting phenomena on a solid surface with a nanometer-scale slit pore. The simulations used the Lennard-Jones potential for the liquid molecules and the solid atoms in order to examine the fundamental mechanisms of the wetting phenomena qualitatively, and investigated how the width of the slit pore and the liquid-solid interactions influence the dynamic phenomena of liquid molecules in the vicinity of the slit pore. The model employed in the present simulation system, a solid surface with a slit pore, is often seen in the manufacturing processes of semiconductor devices [1,8,9].

Numerical methods

Figure 1 shows the calculation model in the present study. The calculation region above the slit pore is $10.08 \times 10.08 \times 15.00 \text{ nm}^3$, and the region of the slit pore is $L \times 10.08 \times 5.04 \text{ nm}^3$, where L represents the width of the slit pore, and is varied as one of the calculation parameters in the present study. Periodic boundary conditions are employed in the x and y directions and the mirror boundary condition [10] is used at the top of a unit cell. The solid wall in the Figure consists of three solid layers where the outermost layer is fixed and the temperature of the middle layer is controlled at a constant value of 100 K by the Langevin method [11,12]. An ensemble of 7500 solid atoms are arrayed in a fcc lattice structure with the (111) surface in contact with the liquid molecules in the unit cell. The

solid wall potential parameters are taken to be those of platinum(Pt) and the liquid is assumed to be argon(Ar).

All interactions between molecules or atoms are assumed to obey the 12-6 Lennard-Jones potential, of the form,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the distance between particles. The parameters for the liquid-liquid(Ar-Ar) interaction employed are $\sigma_{Ar} = 3.40 \text{ \AA}$ and $\epsilon_{Ar} = 1.67 \times 10^{-21} \text{ J}$, respectively [4,6]. The Lennard-Jones parameters, $\sigma_{Pt} = 2.54 \text{ \AA}$ and $\epsilon_{Pt} = 109.2 \times 10^{-21} \text{ J}$ in the reference [13] are used for the solid-solid(Pt-Pt) interaction. The interaction between the liquid molecules and the wall atoms is also described by the Lennard-Jones potential form, and the Lorentz-Berthelot combining rule is applied to obtain the standard parameters σ_{Ar-Pt} and ϵ_{Ar-Pt} . For controlling the liquid-solid interaction intensity, the relative parameter α is adopted in addition to the standard value ϵ_{Ar-Pt} in the calculation. Hence, the potential energy between the liquid molecules and the wall atoms can be written as,

$$\phi_{Ar-Pt}(r) = 4\alpha\epsilon_{Ar-Pt} \left[\left(\frac{\sigma_{Ar-Pt}}{r} \right)^{12} - \left(\frac{\sigma_{Ar-Pt}}{r} \right)^6 \right]. \quad (2)$$

As an initial condition, a liquid film consisting of 12960 liquid molecules(Ar) exists on the solid wall(Pt) with a slit pore as shown in Fig. 1. The liquid film is initially kept at 100 K by the velocity scaling control for 100.0 ps, followed by 1.0 ns of the relaxation calculation conducted to equilibrate the system without the velocity scaling control(NVT ensemble). 3σ is used for the cut-off radius. The number density of the bulk part of the liquid film at 1.0 ns is $1.9 \times 10^{28} \text{ m}^{-3}$ and the system is initially in gas-liquid equilibrium at 100 K [14,15]. During the relaxation calculation, the value of α is

set to be 0.03, a relatively lower interaction intensity compared with the values employed for the observation of the wetting phenomena. After the relaxation calculation, the interaction parameter α is changed to the target value and the nonequilibrium classical molecular dynamics (NEMD) simulations are conducted for at least 1.0 ns.

Results and discussions

Effects of the liquid-solid interaction on the wetting phenomena

Figures 2(a) and (b) show typical calculated results for two cases, both with $L = 4.2$ nm. In Fig. 2(a), the inside of the slit pore is unfilled with liquid molecules at $t = 1.0$ ns, while in Fig. 2(b) the pore filling is in progress, and is completed at $t = 1.0$ ns. When the liquid-solid interaction intensity is relatively low ($\alpha = 0.03$), the filling of the liquid molecules into the inside of the slit pore doesn't occur as completely as the results given by the NEMD during 10.0 ns. Meanwhile, the filling of the liquid molecules into the slit pore occurs only when the value of α exceeds a certain value. Figure 2(b) shows the filling-in progress when the time, t , is 150.0 ps. These results show the wetting phenomenon of the slit pore, i.e., whether or not the inside of the slit pore is filled with the liquid molecules within a definite time, depends on the liquid-solid interaction intensity.

The simulation results of the slit pore wetting obtained by changing the value of α are listed in Table 1. The wetting probability in Table 1 is defined as the result which shows whether the inside of the slit pore is filled with liquid molecules within 1.0 ns. A white circle indicates that the inside of the pore was filled with the liquid molecules within 1.0 ns, a white triangle is the case when the filling wasn't completed within 1.0 ns, and a cross indicates a low probability of the filling in the calculation during 1.0 ns.

The results indicate that there is a critical value of $\alpha (= \alpha_c)$ which determines whether the inside of the slit pore is filled with the liquid molecules within a definite time.

Figure 3 shows the time evolution of the number of liquid molecules inside the slit pore for various values of the interaction intensity α (0.04 – 0.09). The initial number of argon molecules inside the slit pore is subtracted from the total number of liquid molecules in Fig. 3. When the value of α is relatively low (0.04), there is little deviation in the number of liquid molecules inside the slit pore, and the initial state is stable for at least 1.0 ns. Changing the value of α to 0.05, the number of the liquid molecules inside the slit pore fluctuates, although there seems to be little possibility of complete wetting, judging from the simulation results for 1.0 ns. When the value of α is sufficiently high (0.07, 0.08, and 0.09), the wetting phenomenon of the slit pore is completed within 1.0 ns. These results also suggest that the wetting phenomena, whether or not the inside of the slit pore is filled with liquid molecules within 1.0 ns, as well as the characteristic time of the filling phenomena, are dependent on the liquid-solid interaction intensity α in the present calculation, in which the liquid-solid interaction is assumed to obey Eq. (2).

The effects of the liquid-solid interaction intensity α on the progress of wetting phenomenon are shown in Fig. 4. Figures 4(a) and (b) indicate that the liquid-solid interaction intensity α has a considerable effect on wetting progress; it can be seen that the higher the interaction intensity α , the more that the filling is driven by the liquid molecules in the vicinity of the solid wall, and the greater the curvature of the gas-liquid interface tends to become. When the value of α is relatively high as shown in Fig. 4(c), it can be seen more clearly that a monolayer is formed on the wall surface before the bulk part of the liquid molecules proceeds into the slit pore.

The wetting process completion time when the value of α is changed is shown in Fig. 5. The wetting process completion time used in Fig. 5 is defined as the time when the number of liquid molecules inside the slit pore reaches 95% of the final (or equilibrium) value. 10 simulations are conducted for each value of α , and the initial values are chosen at intervals of 50.0 ps after the relaxation calculation. The result shows that when the value of α is relatively low (0.07-0.10), the wetting process completion time decreases with the increase of α . On the other hand, at values of $\alpha > 0.10$, the completion time does not show pronounced differences in changes in α . This could be due to the formation of a monolayer which precedes the bulk part of the liquid molecules in the slit pore wetting process, and the arrangement of the liquid molecules in the vicinity of the wall surface as shown in Fig. 7. In the case of $\alpha > 0.10$, the monolayer is first formed inside the slit pore by the high interaction intensity with liquid molecules before the bulk part of the liquid molecules proceeds into the slit pore, and the bulk liquid becomes less directly affected by the liquid-solid intensity. Effects of temperature are investigated and shown in Fig. 6. The profiles of the curves are qualitatively the same when the temperature ranges from 85 to 100 K.

Effects of the slit pore width on the wetting phenomena

To examine the effects of the slit pore width L on wetting phenomena, the calculations were conducted with changing L from 0.6 to 4.2 nm while the value of α was kept constant at 0.08. Figure 8 clarifies the effect of changing L on the slit pore wetting completion time. The completion time used in Fig. 8 is the same as that used for Fig. 5. In the case of $L < 2.2$ nm, the completion time of the wetting process decreases with decreasing slit pore width. This effect is due to the change of the potential field inside of the slit pore depending on pore width. The potential field inside the slit pore decreases

when the slit pore width drops below a certain value.

The critical values of $\alpha(= \alpha_c)$ are defined as the values which determine whether the inside of the slit pore is completely filled with the liquid molecules during the 1.0 ns calculation. The values of α_c for each pore width L can be estimated from the results shown in Table 2. The meanings of the marks in Table 2 are the same as those in Table 1. In the case of $L < 2.2$ nm, the wetting phenomenon occurs even though the value of α is relatively low (0.05 or 0.06). From the results shown in Table 2, the critical value α_c is changeable depending on the pore width. The potential field inside the slit pore decreases and the liquid molecules are allowed to enter the slit pore when the pore width drops below a certain value under the present calculation condition.

Conclusions

Molecular dynamics simulations were conducted for the liquid wetting phenomena on a solid surface with a nanometer-scale slit pore, with the objective of investigating how the width of the slit pore and the liquid-solid interactions influence the dynamic phenomena of liquid molecules in the vicinity of the slit pore. The interactions between liquid molecules and solid atoms are modeled as van der Waals forces described by 12-6 Lennard-Jones potential functions. The main findings in the present study are as follows:

- (1) The wetting phenomena of the slit pore, i.e., whether the inside of the slit pore is filled with liquid molecules within a definite time, as well as the characteristic time of the phenomena, are dependent on the intensity of the liquid molecule–solid atoms interaction.
- (2) The completion time of the slit pore wetting process tends to become short when the interaction intensity between liquid molecules and solid atoms is relatively

high.

- (3) When the slit pore width L is relatively narrow, i.e., when $L < 2.2$ nm under the present conditions, the wetting completion time is dependent on L .
- (4) The critical value of the interaction intensity between the liquid molecules and wall atoms which determines whether the inside of the slit pore is filled with the liquid molecules is changeable depending on the slit pore width.

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Nomenclature

<i>Ar</i>	argon
<i>L</i>	width of the slit pore
<i>Pt</i>	platinum

r	distance between molecules or atoms, Å
t	time, sec
T	temperature, K
x, y, z	coordinates of the system; see Figure 1

Greek Symbols

α	liquid-solid interaction intensity
α_c	critical liquid-solid interaction intensity
ε	Lennard-Jones potential parameter, J
ε_{Ar}	Lennard-Jones potential parameter between argon molecules, J
ε_{Pt}	Lennard-Jones potential parameter between platinum atoms, J
ε_{Ar-Pt}	Lennard-Jones potential parameter between argon molecule and platinum atom, J
σ	Lennard-Jones potential parameter, Å
σ_{Ar}	Lennard-Jones potential parameter between argon molecules, Å
σ_{Pt}	Lennard-Jones potential parameter between platinum atoms, Å
σ_{Ar-Pt}	Lennard-Jones potential parameter between argon molecule and platinum atom, Å
φ	potential function between argon molecules, J
φ_{Ar-Pt}	potential function between argon molecule and platinum atom, J

Subscripts

Ar argon

Ar-Pt argon-platinum

c criticality

Pt platinum

Figure 1. Calculation model (initial condition). Periodic boundary conditions are employed in the x and y directions and the mirror boundary condition is used at the top of the unit cell.

Figure 2. Typical calculation results when the inside of the slit pore isn't filled or is filled with liquid molecules in the case of $L = 4.2$ nm: (a) $\alpha = 0.03$ ($t = 1.0$ ns) and (b) $\alpha = 0.08$ ($t = 150.0$ ps).

Figure 3. Time evolution of the number of liquid molecules inside the slit pore for various interaction intensity α .

Figure 4. Effect of the liquid-solid interaction intensity on the distribution of liquid molecules when the wetting phenomenon occurs: (a) $\alpha = 0.07$, (b) $\alpha = 0.08$, and (c) $\alpha = 0.10$.

Figure 5. Effect of the liquid-solid interaction intensity on the completion time of the slit pore wetting process in the case of $T = 100$ K. The completion time is defined by the variation of the total number of the liquid molecules inside the slit pore.

Figure 6. Effect of the liquid-solid interaction intensity on the completion time of the slit pore wetting process in the case of $T = 85, 90, 95$, and 100 K.

Figure 7. Typical configurations and the liquid molecular arrangement during the wetting phenomenon in the case of $\alpha = 0.20$: (a) $t = 100.0$ ps, (b) $t = 200.0$ ps, and (c) $t = 500.0$ ps.

Figure 8. Effects of the slit pore width on the completion time of the wetting phenomenon in the case of $\alpha = 0.08$.

FIGURES ONLY.

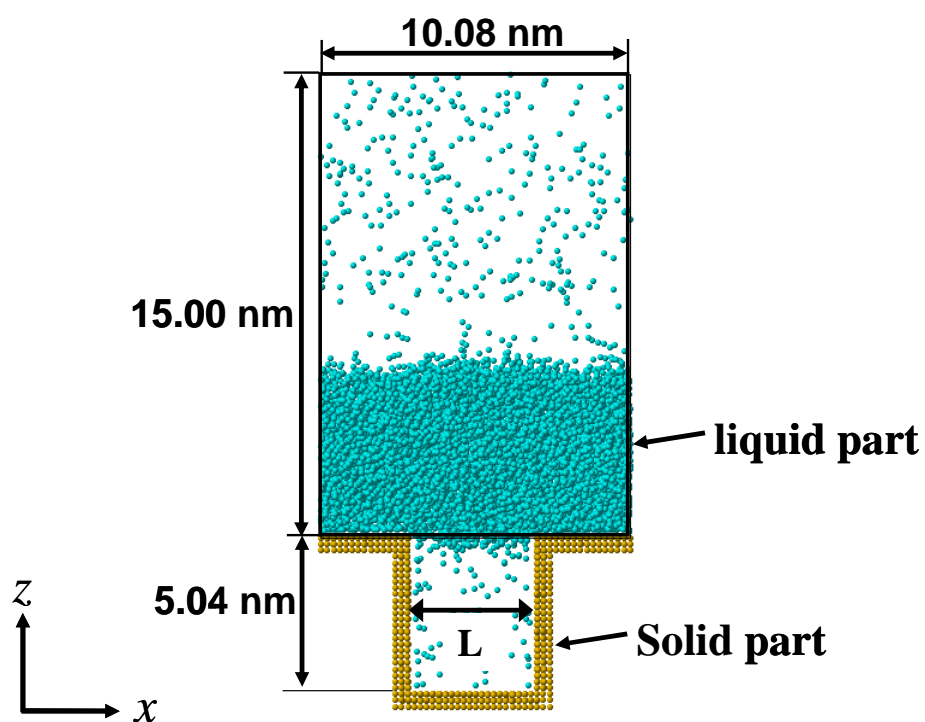


Figure 1.

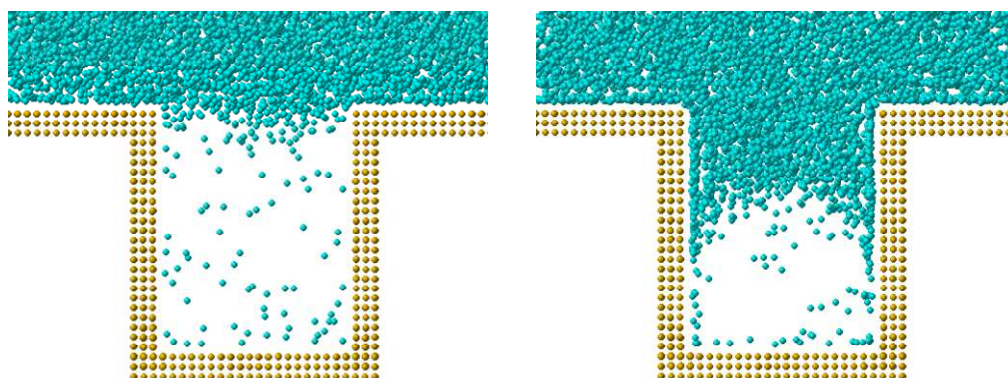


Figure 2.

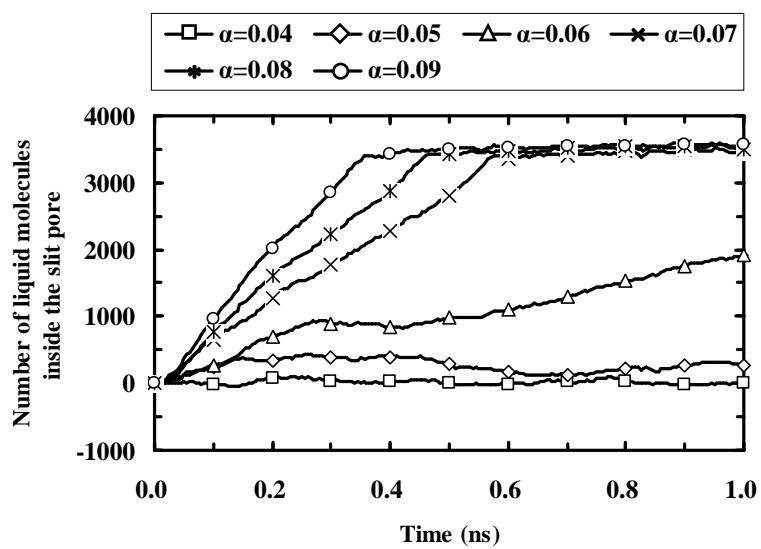


Figure 3.

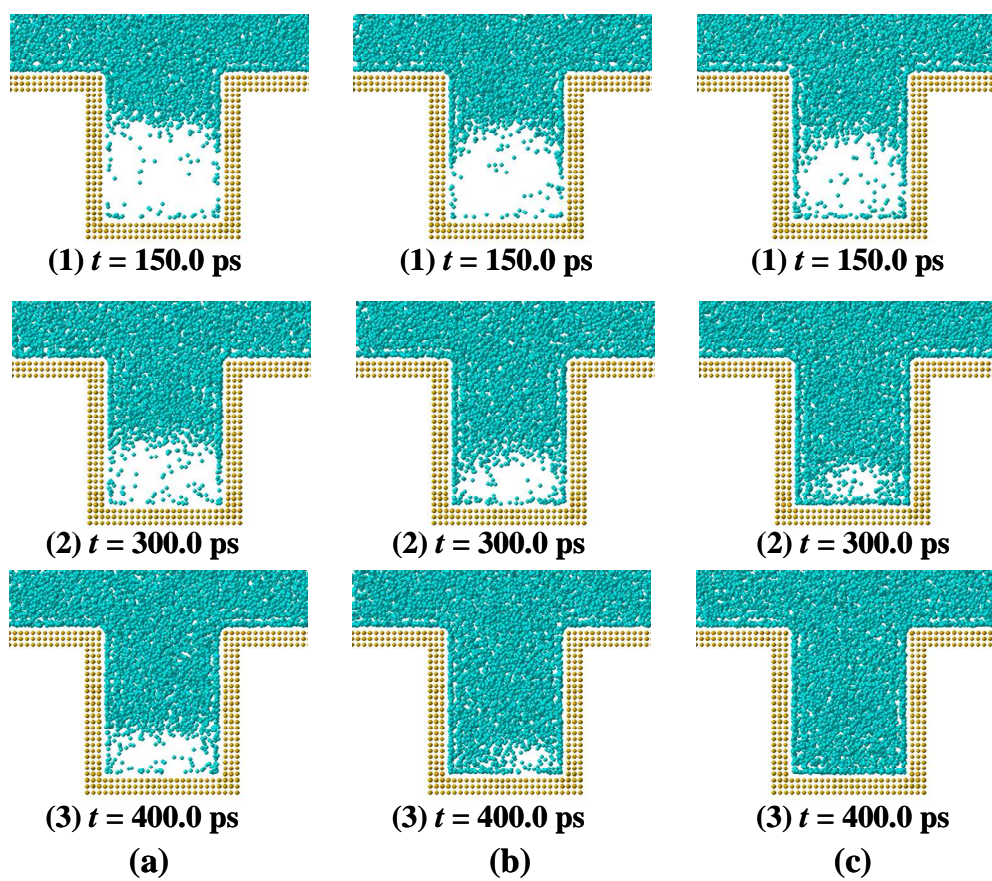


Figure 4.

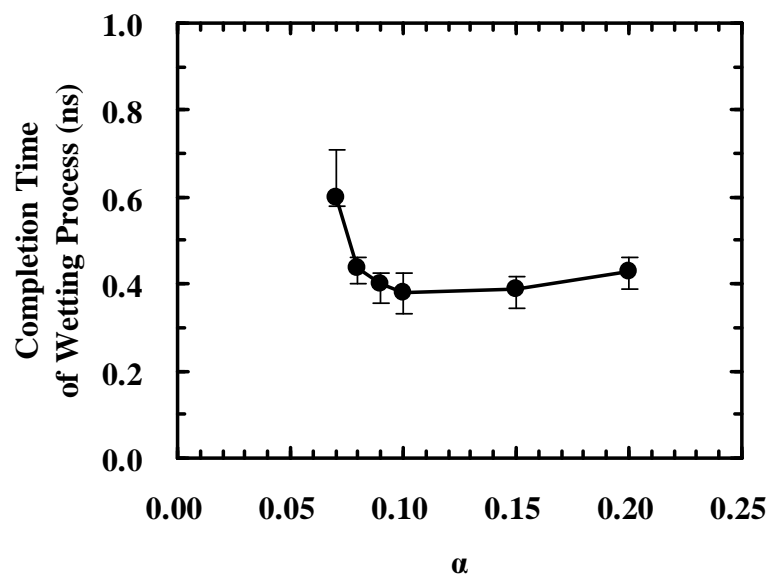


Figure 5.

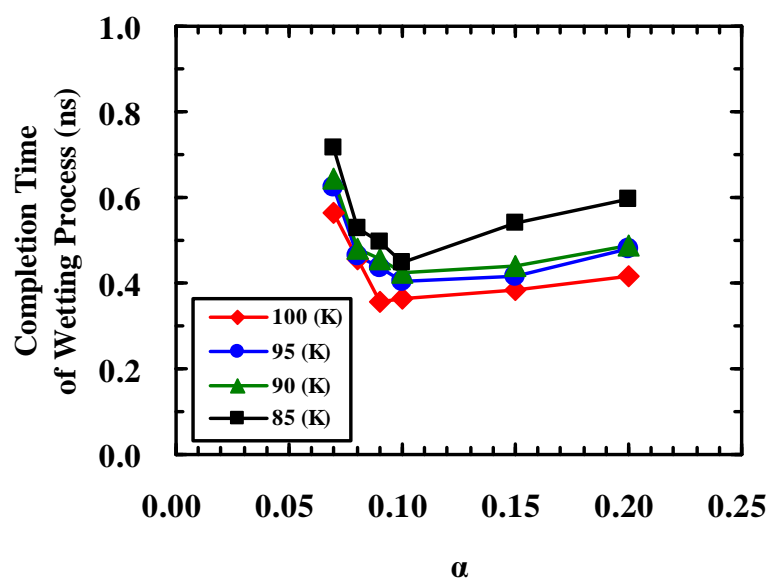


Figure 6.

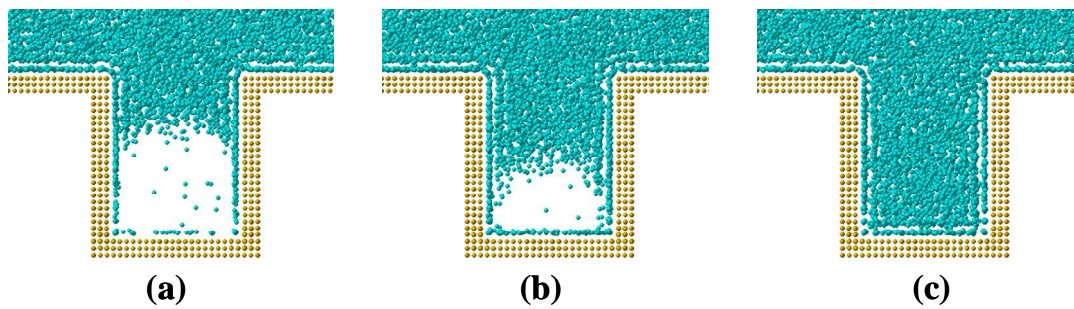


Figure 7.

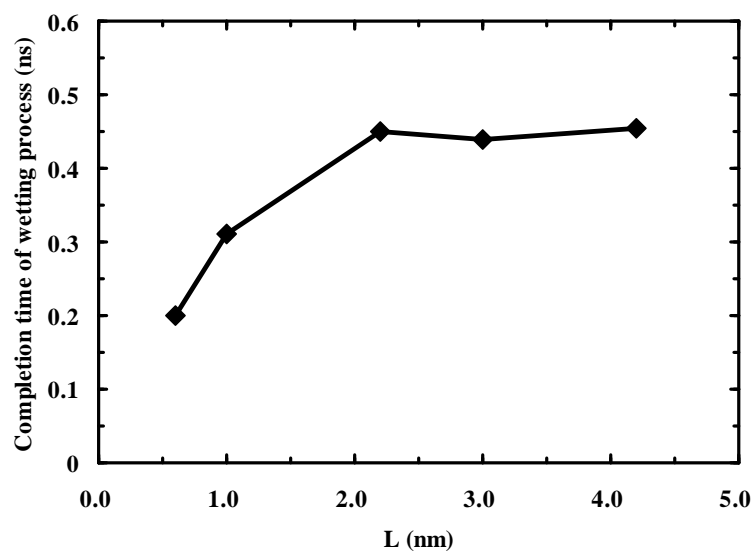


Figure 8.

Table 1. The α value and wetting probability.

α	Probability of wetting phenomenon
0.03	×
0.04	×
0.05	△
0.06	△
0.07	○
0.08	○
0.09	○
0.10	○

The white circle indicates that the inside of the pore was filled with the liquid molecules within 1.0 ns, the white triangle is the case when the filling wasn't completed within 1.0 ns, and the cross indicates a low probability of the filling in the calculation during 1.0 ns.

Table 2. The effects of pore width and α value on wetting probability.

α	L (nm)					
	0.6	1.0	2.2	3.0	4.2	5.0
0.04	×	×	×	×	×	×
0.05	○	×	×	×	×	×
0.06	○	○	△	△	△	△
0.07	○	○	○	○	○	○

The Table shows the effects of the pore width L and the value of α on the probability of the wetting phenomenon of the slit pore. The symbols used in the table have the same meaning as in Table 1.