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KINETIC MODEL FOR MOLECULAR TRANSPORT OF LIQUID MIXTURES IN THE VICINITY OF SOLID-LIQUID INTERFACES

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ABSTRACT

In order to establish a kinetic model that describes the dynamic behavior of liquid molecules moving across liquid-solid surfaces, simple systems consisting of the solid wall and liquid mixtures were applied. Using these systems, MD simulation was performed in which molecular transport associated with adsorption and desorption of liquid molecules onto the solid surfaces were analyzed. In the vicinity of the solid-liquid interface, the density distributions exhibit well-known multiple peaks, which indicates adsorption layers are formed due to solid-liquid interaction. In our model, the molecular transport among the adsorption layers perpendicular to the walls is considered as a kinetic process mediated by molecular hopping which surmounts a free energy barrier between the layers. In this model, the mobility of molecules is expressed as a reaction rate constant of this kinetic process, and then the theoretical relation holds between the height of the barrier and the reaction rate constant. The validity of the kinetic model, which describes the relationship between obtained reaction constants and measured free energy barrier, was examined, comparing the molecular transport observed by MD simulations for liquid mixtures with various molar fractions. A good agreement was found between the theoretical relationships and the observations in the MD simulation.

KEY WORDS: Nano/Micro scale measurement and simulation, Molecular transport, wet nanolithography

1. INTRODUCTION

There is an increasing need in current technologies to understand and control nanoscale mass transport phenomena in liquids adjacent to solid surfaces. For example, lithographic techniques applying under 10 nm pattern on semiconductor wafer substrates are now being developed [1-2]. In the wet processing involved in such semiconductor fabrication, it is required to impregnate the patterning with chemical solutions and to transport the functional molecules to the solid interface. However, the mass transport in such situations cannot be predicted by a straightforward extension of those at macroscopic scales. It is widely known that liquid molecules form ordered structures in the vicinity of solid-liquid interfaces. Since these structures have dominant influences on the mass transport in the solid-liquid interface region, the transport shows anomalous features that differ from the features of ordinary diffusion following Fick's law. So, it is difficult to explain mass transport phenomena of heterogeneous liquid in nanoscale as a molecular diffusion model following Fick's law based on diffusion equations.

In order to analyze the mass transport phenomenon in the heterogeneous liquid, there are some studies which predict the behavior of the molecule by measuring PMF (potential mean force) [3] distribution. The molecular adsorption and desorption phenomenon perpendicular to the interface in the vicinity of the solid wall, the relation between the free energy barrier to the molecular movement obtained from the PMF distribution and the transport

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of the molecules moving the adsorption layers beyond the barrier has been quantitatively examined by using Ar monatomic fluid [4]. However, the technique like liquid replacement and surface modification are mostly used in the liquid mixture, and therefore it is required to confirm the validity of the above relation in the case of liquid mixtures. In the mass transport of the liquid mixture perpendicular to the interface, there is an influence on the composition of the molecules constituting the system and the adsorption structure, so there is a room for consideration about the validity of the above theory for pure liquids.

Here, a molecular dynamics (MD) simulation was performed in which the PMF distribution and dynamics of molecular adsorption and desorption in liquid mixture onto the solid surface were analyzed and the influence of mixed liquids on the molecular adsorption onto the solid surface was discussed.

2. COMPUTATIONAL DETAILS

We performed MD simulations of liquid mixture of Ar and Kr between two model solid walls as shown in Fig. 1. The interaction between two liquid molecules is given by the Lennard-Jones (LJ) potential,

$$\phi(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{1}$$

where r is the parameter of distance between molecules, and ε_{Ar} =1.653×10^{-21} J, σ_{Ar}=3.4236 Å for Ar [5], ε_{kr} =2.250×10^{-21} J, σ_{Ar} =3.650 Å for Kr [6] were used for the parameters. From the Lorentz-Berthelot rule, the parameters between Ar-Kr particles were determined as $\varepsilon_{Ar\text{-}Kr}$ =1.929×10^{-21} J and $\sigma_{Ar\text{-}Kr}$=3.5368 Å. The molar mass was 39.95 kg/kmol for Ar and 83.80 kg/kmol for Kr. The cut-off distances for these intermolecular potentials were set to be 16Å.

To make simple solid walls on which liquid molecules form adsorption layers, the interaction between liquid molecules and a solid wall is expressed as a function of only the distance between a solid surface and a liquid molecule. A functional form of the wall potential, U(D) is given by [4]

$$U(D) = \frac{3\sqrt{3}}{2}\varepsilon_e\left\{\left(\frac{\sigma_e}{D}\right)^{9} - \left(\frac{\sigma_e}{D}\right)^{3}\right\} \tag{2}$$

$$\varepsilon_e = \frac{2\sqrt{10}}{9}\pi\varepsilon_w, \quad \sigma_e = \left(\frac{2}{15}\right)^{\frac{1}{6}}\sigma_w \tag{3}$$

where ε_e and σ_e are the potential parameters for the well depth and the radius, and D is the normal distance between a particle and the wall. This potential is applied between the solid wall and every liquid molecule. It is obtained assuming a flat and smooth (not atomically structured) wall of an effective continuum medium where LJ particles with the parameters of ε_e and σ_e between the solid walls and the liquid molecules are distributed with a uniform density corresponding to the number density of a fcc crystal made by LJ particles. The computational system was composed of two parallel solid walls and the liquid in a computational cell with the size of Lx×Ly×Lz = 50×50×100Å. The two solid surfaces were located at z = 0 and 100 Å, respectively. Periodical boundary conditions were applied in x and y direction.

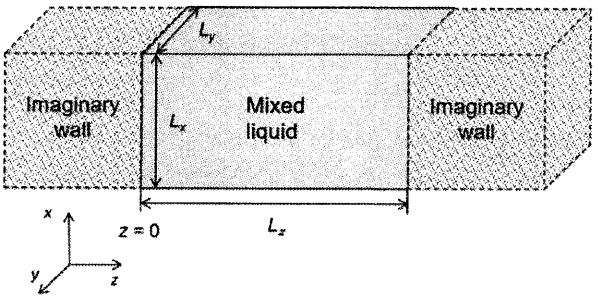

Fig. 1 A schematic of simulation system of liquid mixture between imaginary wall.

In this study, we changed the potential parameter ε_w of the LJ interaction with wall surface the wall surface. In addition, the molar ratio between Ar and Kr in the bulk region was changed and the resulted various systems were analyzed. We tried five parameters for ε_w from 0.8265×10^{-21} J to 3.306×10^{-21} J and the five molar ratios from 0 to 1 for each ε_w, and thus 25 systems in total. The cut off distance of this potential is set to 35 Å. The state of the system is a saturated liquid in the bulk region free from the influences of the solid walls at a temperature 130K. The velocity Verlet algorithm was applied with the time step of 1.0×10^{-15}s. The simulation data was acquired in the NVE ensemble for 12,000,000 steps after an equilibration run. In this study, velocity scaling was applied at one step in every 10,000 steps to keep the temperature of the system constant.

3. RESULTS AND DISCUSSION

The number density distribution of Ar and Kr molecules under the condition of $\varepsilon_w = 1.653\times10^{-21}$ J and Ar molar ratio 0.25 is shown in Fig 2. The distribution of number density exhibits oscillatory behavior near the solid walls, which shows the well-known layered structure of liquid molecules pinned by the solid wall. Hereafter, the adsorption layers nearest to the solid surface are referred to as 1st adsorption layer, 2nd adsorption layer and 3rd adsorption layer from the wall side toward the bulk liquid. Among the adsorption layers mentioned above, hopping migration of the liquid molecules occurs under the significant influence of the layered structures, and therefore mass transport in the vicinity of walls shown different features from ordinary diffusion. Considering this transport in the presence of heterogeneities of density as a kinetic process, the transport process was analyzed in the framework of reaction kinetics.

In our model [4], the mass transport among the adsorption layers perpendicular to the walls is considered as a kinetic process mediated by molecular hopping that surmounts a free energy barrier between the layers. In this theoretical model, the mobility of molecules is expressed as a reaction rate constant of this kinetic process, and then the Arrhenius equation holds between the height of the barrier and the reaction rate constant. The Arrhenius equation is given by

$$k = k_0 \exp\left(-\frac{\Delta F}{k_B T}\right) \tag{4}$$

where k, ΔF, k_B, T and k_0 denote the reaction rate constant, height of the free energy barrier, the Boltzmann constant, temperature and frequency factor, respectively. Here the free energy profile with respect to molecular migration perpendicular to the wall is evaluated by the PMF. The distribution of the PMF in the system consisting of a single component is given by

$$F(z) = -k_B T \ln\left(\frac{\rho(z)}{\rho_0}\right) \tag{5}$$

where $F(z)$, $\rho(z)$ and ρ_0 denote the free energy, number density at coordinate of position z and number density in

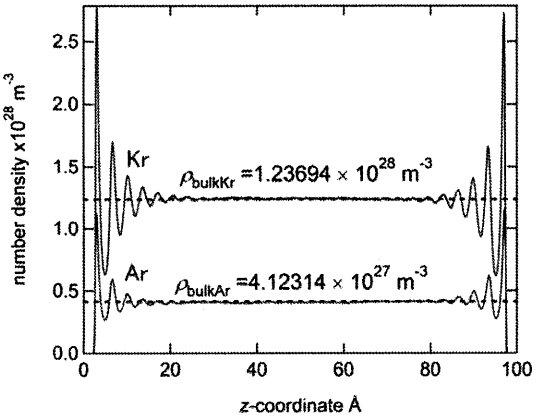

Fig.2 Number density distribution between the effective continuum walls. The black dotted straight lines indicate the number densities of saturated liquids of Ar and Kr under the test temperatures. The number densities of Ar and Kr are plotted as the red and blue lines, respectively.

bulk liquid, respectively. In this study, since the target is the liquid mixture of Ar and Kr, the equation is applied to Ar and Kr respectively. From the equation (5), the height of free energy barrier ΔF which liquid molecule surmounts when it moves to the adjacent adsorption layer is obtained by

$$\Delta F = -k_B T \ln\left(\frac{\rho_{max}}{\rho_{min}}\right) \tag{6}$$

where ρ_{max} is the maximum density in the present layer and ρ_{min} is the minimum density between the present layer and the adjacent one. In the adsorption and desorption model based on the equation (4), the linear relation shown in the equation (7) holds from the equations (4) and (6).

$$k_{ij} = k_0 \frac{\rho_{max}}{\rho_{min}} \tag{7}$$

where k_{ij} denotes the reaction rate constant when liquid molecule moves from the adsorption layer i to the adsorption layer j. When the frequency factor k_0 differs in each molecular migration process, it is considered as a frequency factor k_{0i} in the process of desorption of molecules from the adsorption layer i, and the Eq. (7) can be transformed into

$$\frac{k_{ij}}{k_{0i}} = \frac{\rho_{max}}{\rho_{min}} \tag{8}$$

The frequency factor when Ar and Kr molecules surmount a one-dimensional barrier in the z direction can be expressed as follows based on the transition state theory [7-8].

$$k_{0i}(T) = \frac{k_B T}{h Q^R(T)} \tag{9}$$

$$Q^R(T) = \sqrt{\frac{M k_B T}{2\pi\hbar^2}} \int_{well,i} \exp[-[F(z) - F_{min}]/k_B T] dz \tag{10}$$

where Q^R, M, h, and $\hbar$ denote the distribution function of the reactant (which in this study, corresponds to that of the liquid molecule before surmounting the free energy barrier), the mass of one molecule, the Planck's constant, and Planck's constant divided by 2π, respectively. Also, "well, i" in the integration range indicates a region from the local maximum value of the PMF in the adsorption layer i to the local maximum value in the adsorption layer which is next to the layer i.

The reaction constant k corresponding to molecular mobility among adsorption layers is obtained from the molecular transport observed in the MD simulations. Here, the mobility of molecules migrating to the neighbor layer is evaluated quantitatively using the survival probability shown below [4]. The probability of molecules in a certain region is given by

$$P_s(t_s) = \frac{N(0, t_s)}{N(0)} \tag{11}$$

where $N(0)$ is the number of molecules which exist in the region at an initial time $t = 0$, and $N(0, t_s)$ is the number of molecules that continue to exist in that region from time 0 to t_s second later. Since the survival probabilities of molecules in adsorbed layers decay exponentially with t_s, k_{tot} is obtained using exponential curve fitting as follows,

$$P_s(t_s) = \exp(-k_{tot} t_s) \tag{12}$$

In addition, to know the mobility of liquid molecules among the layers, the direction of the molecular migration, toward the wall or the bulk side, was observed in the simulation, and the number of molecules moving towards each side was individually counted. The reaction constant of the process in which molecules migrate to the neighboring layers toward the wall and the bulk side is obtained, which is specifically the value representing the mobility, as follows.

$$k_{wall} = \frac{N_{wall\infty}}{N_{wall\infty} + N_{bulk\infty}} k_{tot} \tag{13}$$

$$k_{bulk} = \frac{N_{bulk\infty}}{N_{wall\infty} + N_{bulk\infty}} k_{tot} \tag{14}$$

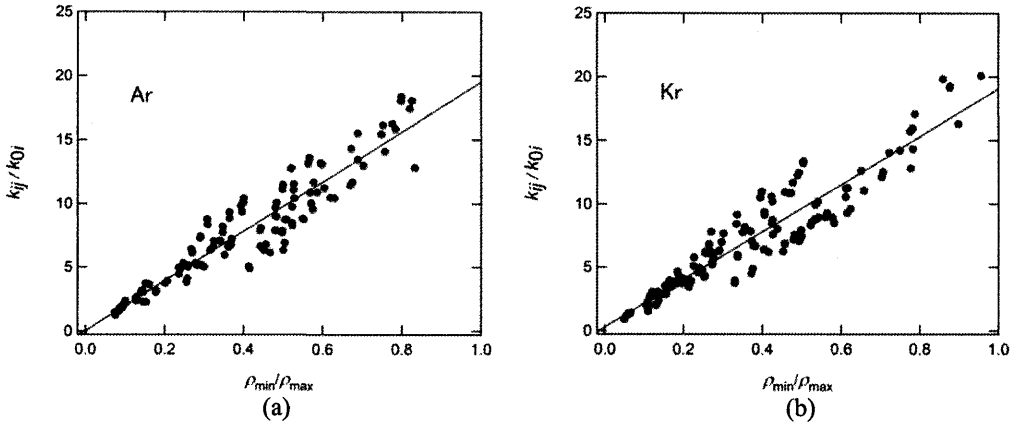

Fig.3 Values of k_{ij} / k_{0i} as a function of ρ_{min} / ρ_{min} for (a) Ar and (b) Kr. The straight lines are determined by the least square fitting.

where k_{wall} and k_{bulk} are the reaction rate constants of the process of liquid molecules migrating to neighboring layers toward the wall and the bulk side, respectively. Now, we examine the validity of the present model in the liquid mixtures by seeing whether Eq. (8) holds among obtained reaction constants and measured free energy barriers. Fig. 3 (a) and (b) represent the relationships between k_{ij} / k_{oi} and ρ_{min} / ρ_{max} in Ar and Kr, respectively. Fig. 4 shows data obtained from three types of adsorption / desorption processes which corresponds to the molecular migration from 1st adsorption layers to 2nd adsorption layers, 2nd adsorption layers to 1st adsorption layers, and 2nd adsorption layers to 3rd adsorption layers. In this figure, since the deviation of data points from the approximated linear line is relatively large, it is hard to confirm the validity of Eq. (8). In the transition state theory, it is assumed that the product does not return to the state before the reaction after surmounting the transition state. However, in the mass transport between the adsorption layers, it occasionally happens that the molecules that surmount the transition state immediately return to the original adsorption layer (re-crossing). The scattered data from the theoretically predicted linear trend is partly because the occurrence of this re-crossing is different among the conditions with the systems having different molar ratios, and it influences the migration rate between the layers. Therefore, the obtained data were divided into those for each molar fraction, and these were linearly approximated. As shown in Fig.4 (a) and (b), all the data corresponding to each molar ratio is well fitted by the linear line passing near the origin and the relation between the reaction rate constant and the free energy barrier can be explained well by Eq. (8) when the data are divided into those for each molar fraction.

It is concluded from these results that in the liquid mixture in the vicinity of an effective medium wall, the molecular transport perpendicular to the wall can be described when the data are divided into those for each composition as the migration model governed by the Arrhenius equation based on the reaction kinetics, where the liquid molecule exits a stable energy state and migrates by surmounting a free energy barrier.

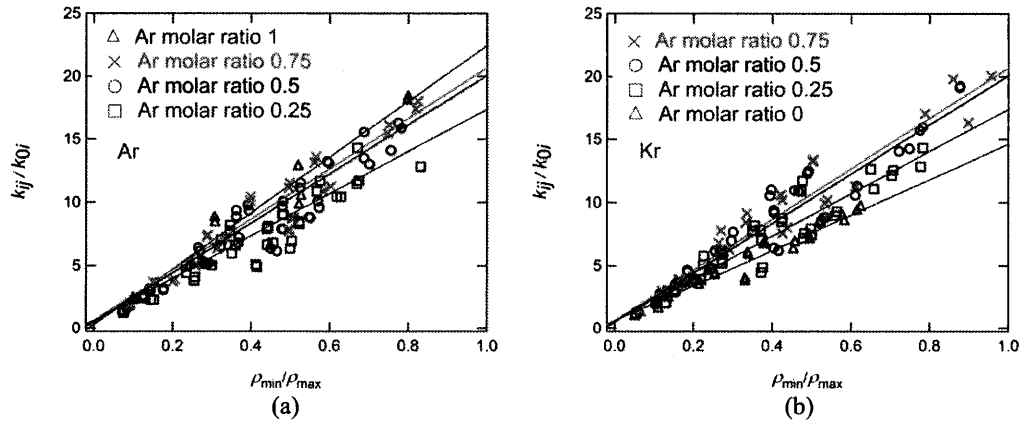

Fig.4 Values of k_{ij} / k_{0i} as a function of ρ_{min} / ρ_{min} with different marks and colors for the Ar molar ratios for (a) Ar and (b) Kr. The straight lines are determined by the least square fitting.

4. CONCLUSIONS

In this study, we aimed to elucidate the mass transport characteristics in liquid mixture affected by solid walls in nanoscale structures. We constructed a model in which the molecular migration between adsorption layers formed by interaction between liquid molecules and solid walls. This kinetic model is based on the kinetic process in which molecules move due to thermal motion beyond the energy barriers existing between adsorption layers. The validity of the theoretical model was verified by obtaining the energy barrier and the rate constant from the result of MD simulations. Concerning the transport of molecules in a liquid mixture adjacent to a solid surface, a kinetic model to describe adsorption and desorption was well explained by the Arrhenius equation when the data are divided into those for each composition. From this result, the effectiveness of the present kinetic model for the migration of liquid molecules between adsorption layers, which is explained based on a view that the molecule migrates over a certain height of free energy barrier evaluated by using PMF, was confirmed. The present result contributes to a better understanding and control of the molecular transport in complex liquid-solid systems, which is essential for the development of wet nanofabrication processes. It is in progress that, this kinetic model is examined in depth for more realistic systems so that it can be utilized to engineering and industrial applications.

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