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Molecular dynamics analysis of the wetting front structure in metal/metal systems

A. KUBO, T. MAKINO*, D. SUGIYAMA, S.-I. TANAKA
Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
E-mail: makino.takehiko@nitech.ac.jp

We developed two-body potentials based on *ab initio* molecular orbital calculations, and used these to perform molecular dynamics calculations of wetting in the Al/Cu, In/Cu and Zn/Cu systems in order to clarify the structure of the wetting front. To optimize the description of liquid/solid interface energetics, it was found that the interatomic potentials differed for the surfaces having different crystal orientations, even in the cases of the same pairs of elements. Different interaction energetics resulted in a difference in the wetting behavior on the (100) and (111) surfaces. A precursor film appeared in the nonreactive system, and the condition for film formation was estimated.

1. Introduction

Wetting is a well-known phenomenon utilized in various fields. Recently, it has been applied to the formation of interfaces for electronic devices and functional surfaces. However, the interface formation has not been well controlled in wetting techniques, although its applicability has been widely extended. It is essential to understand the mechanism of the interface formation in order to achieve control of the structure. The study of wetting has long been in progress, and it has been summarized systematically [1]. The formation of a precursor film having nanometer thickness has been well known as a dynamic phenomenon at the interface since the early 20th century [2], but it has not been clarified what the structure is, or why it forms. There have been some studies that have captured the dynamics of the film structure by various different methods [3, 4], and these studies showed a similar result; that is, that the liquid spread after the film extension. What role the film plays in the wetting has also received attention. However, the atomistic structure of the wetting interface has not been clarified owing to the difficulty of its direct observation. As a useful method of analysis in the investigation of the interface, molecular dynamics (MD) calculations have been used [5–7]. MD calculations trace the motion of atoms; therefore, they are effective for analyzing wetting as it is concerned with the atomistic kinetics. In the recent MD studies of wetting, many-body potentials represented by the embedded atom method (EAM) have been utilized widely. The potentials are constructed by fitting to the physical properties, and can thus describe the atomistic structure within crystals or alloys accurately. However, the liquid-solid potentials used in the studies are arguably not well optimized because the potential fitting included no information about the liquid/solid interface. We conclude that potentials constructed by another approach are required for the description of the wetting systems. In this study, we construct the potentials on the basis of *ab initio* calculations in order to describe the wetting system theoretically, and simulate the wetting processes. The objective is to clarify the wetting front structure and the condition for its formation.

2. Simulation methods

In this work, metal/metal systems were selected to simplify the system and to clarify the changes and their causes. We chose the Cu face-centered cubic crystal structure as a substrate, and Al, In and Zn as liquid atoms. The Cu crystal is suitable as a substrate because the (100) and (111) surfaces do not show any reconstruction [8, 9]. Al, In and Zn are typical alloying elements for Cu alloys, and their melting temperatures (Al: 933 K, In: 430 K, Zn: 693 K) are all lower than that of Cu (1373 K). In many MD studies for wetting systems, the interatomic potentials based on the properties of the bulk solid have been used, and the potentials are not optimized for describing liquid/solid interfaces. However, for describing the wetting systems, the liquid/solid properties are the most important. An optimized potential for liquid-solid interfaces must be determined in a theoretical way since experimental data on the liquid/solid interface does not exist. For modeling the wetting systems, we developed new potentials that fitted to the total energies derived by *ab initio* molecular orbital calculations. We select a two body potential function as the new potential to establish a clear relation

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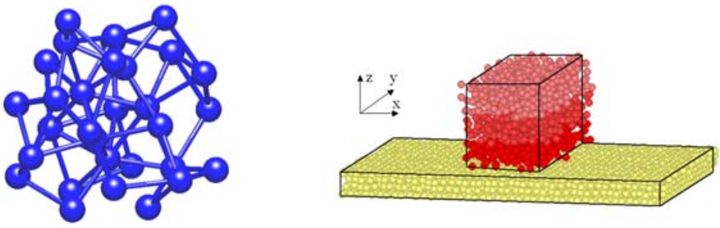
*Authors to whom all correspondence should be addressed.

(a) Cluster for Cu (111) surface (b) Cluster for liquid/solid interface on (111)



(c) Cluster for a liquid state (d) Initial coordination of the simulation

Figure 1 Clusters for (a) Cu (111) surface, (b) liquid/solid interface on (111), and (c) liquid state. (d) is the initial configuration of the MD simulation. The liquid atoms are divided to three layers, an upper layer (light gray balls), a middle layer (gray balls) and a lower layer (black balls).

between the simulation result and interatomic interactions. The Morse type two-body potential function was chosen:

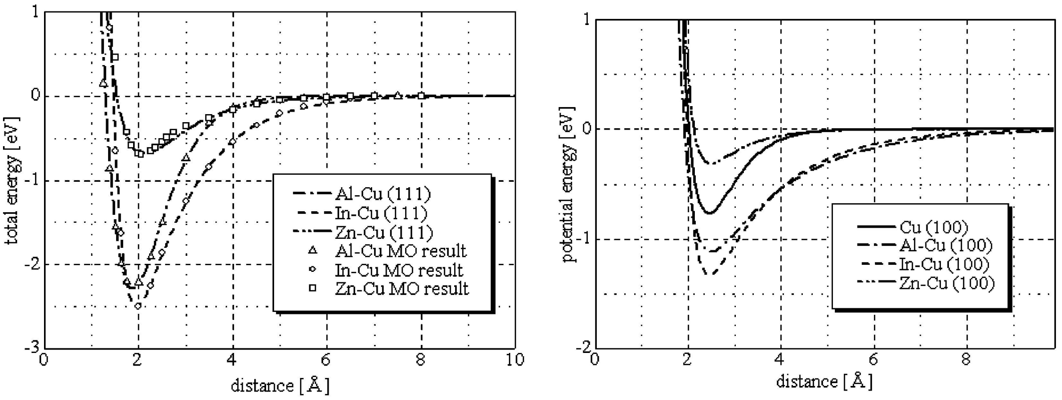
$$\phi(r) = D_1 e^{-\lambda_1 (r - r_0)} - D_2 e^{-\lambda_2 (r - r_0)}, \qquad (1)$$

where D_1 and D_2 are constants with an energy dimension, λ_1 and λ_2 are constants with reciprocal distance dimension, r_0 is a constant of distance dimension and r is interatomic distance. To estimate the total energy, we divided the wetting system into three parts, that is, the surface, solid/liquid interface and liquid state, and assumed clusters that express the states. The clusters are shown in Fig. 1. Fig. 1a shows a cluster that represents a Cu (111) surface. It has a plane shape to express the surface structure. To estimate the interatomic potentials, the interatomic distance of the planar cluster was changed equiaxially and the total energies of the clusters were calculated. Fig. 1b is a cluster of liquid/Cu (111). The black ball represents a liquid atom, and the gray ones represent solid atoms. The liquid atom is arranged at a distance from the substrate. As the distance between the liquid atom and the substrate was changed, the total energy was calculated. The total energies about the Cu (100) surface were calculated in the same way. The fitting procedure employed is as follows: Substituting arbitrary values for the parameters, potential energies are calculated at a coordinate of the clusters. The parameters are determined in order to minimize the differences between the MO calculation results and the potential energies by a least square method to three decimal places. A number of atoms are required for the expression of the liquid state, and it is difficult to fit the parameters from a cluster that has many atoms. The employed method is that the potential parameters are calculated as simultaneous equations that are solved by using sets of coordinates and comparing the total energies. To solve the simultaneous equations, the potential function must not contain the exponential parameter such as Morse type function. We selected a simple 12-6 Lennard-Johnes potential function. Two parameters of the L-J function are given by solving the two simultaneous equations. The liquid cluster used in the *ab initio* calculation is shown in Fig. 1c. The configuration is prepared by MD calculation using the reported empirical potential of alminum [11]. All *ab initio* calculations were executed using Gaussian03W [10] at 3-21G level. An example of fitting result of liquid/Cu (111) interface is shown in Fig. 2a. The potentials fitted to the *ab initio* MO calculations are shown in Fig. 2b and c and the liquid potentials are shown in Fig. 2d. From (b) and (c), we can see that the depths of the potentials between the same pairs are different on the (100) and (111) surfaces. The Cu-Cu potential of the (111) surface is deeper than that of the (100) surface, whereas the Cu-liquid potentials are shallow. The MD calculation was carried out as follows: The initial coordination of the simulation is shown in Fig. 1d. The liquid atoms were classified with three colors tones to clarify the atomic motion in the wetting process, black balls are lower layer atoms, gray balls are middle layer atoms and light gray balls are upper layer atoms. A cut off distance in the MD calculation is about two times of the equilibrium atomic distance. The numbers of Cu atoms are, Al/Cu: 3168, In/Cu: 3520 and Zn/Cu: 3168 on the Cu (100), Al/Cu: 2808, In/Cu: 3024 and Zn/Cu: 2808 on the Cu (111). The number of liquid atoms was 1000. Liquid atoms are installed in the shape of a rectangular parallelepiped and cross the substrate in the y direction. The model melting points of the substrate are about (Cu(100): 2500 K, Cu (111): 3700 K) in the present simulations. The simulations were carried out at 1350 K, far below these temperature and high enough to melt the liquids. The simulation time step was 2 femtoseconds and the total simulation time was 160 picoseconds (ps). Periodic boundary conditions were applied for the x and y directions, and the atoms in the lowest layers of the substrate were fixed.

3. Results

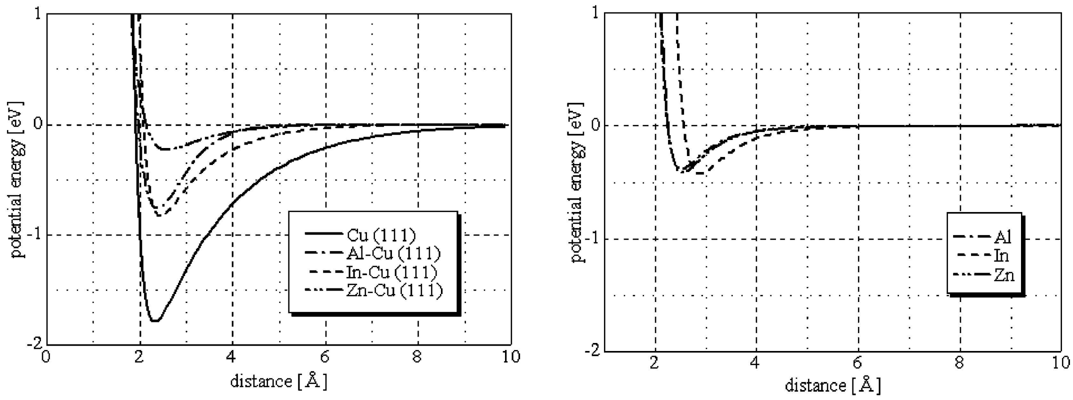
3.1. Wetting on Cu(100) substrate

Fig. 3 shows the simulation results of (a): Al, (b): In and (c): Zn atoms on the Cu (100) surface after 160 ps at 1350 K. On this surface, Al and In atoms show an active exchange of atoms between the solid and the liquid.



(a) Fitting to the MO result of liquid-Cu (111)

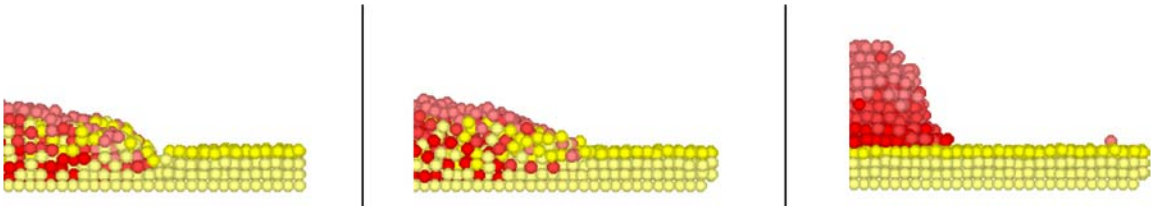
(b) Potential curves on (100)



(c) Potential curves on (111)

(d) Potential curves of Al, In and Zn

Figure 2 Potential fitting result and potential curves fitted to the MO calculation; (a) is an example of fitting to MO result of liquid-Cu (111), (b) shows potentials for Cu-Cu and liquid-Cu on the (100) surface, (c) shows potentials for the (111) surface and (d) shows the potentials for liquids (Al, In, Zn). The depth of the potential is different when the surface crystal orientation is different.



(a) Al/Cu

(b) In/Cu

(c) Zn/Cu

Figure 3 Snapshots of the wetting process of the (a) Al/Cu, (b) In/Cu and (c) Zn/Cu on the Cu (100) surface. Al and In atoms exchanged with atoms in the solid. Zn did not exchange.

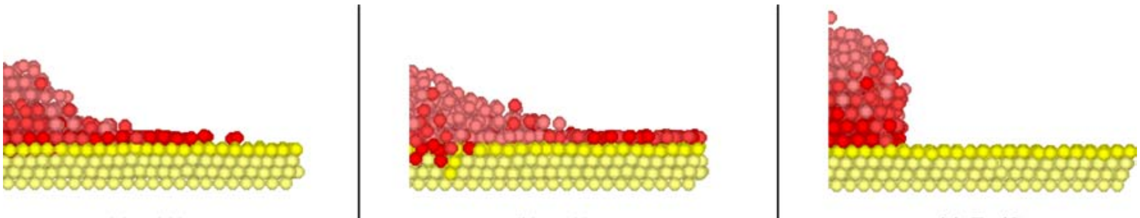
(The numbers of Cu atoms exchanged after 160 ps are Al/Cu: 852, In/Cu: 944 and Zn/Cu: 23.) This wetting behavior can be distinguished as reactive wetting. The liquid atoms are attracted by Cu atoms and pass into the substrate. When the liquid atoms spread, they cover the atoms that already entered the Cu substrate. In contrast, Zn/Cu showed almost nonwetting behavior, and no exchange of atoms occurred between the solid and the liquid.

3.2. Wetting on Cu (111) substrate

Fig. 4 shows the simulation results of (a): Al, (b): In and (c): Zn atoms on the Cu (111) surface after 160 ps at 1350 K. On the (111) surface, Al and In atoms spread more than in the case of the (100) surface. (The numbers of Cu atoms exchanged after 160 ps are Al/Cu: 14, In/Cu: 25 and Zn/Cu: 0.) Exchange of atoms between the solid and the liquid occurred negligibly on this surface. At the wetting front of Al and In, a monolayered film structure that could be distinguished as a precursor film was formed. The film structure consisted of black and gray atoms. The forefront part of the liquid film mainly consists of black balls, while the following part consists of gray balls. Zn atoms did not spread, as was also the case on the Cu (100) surface.

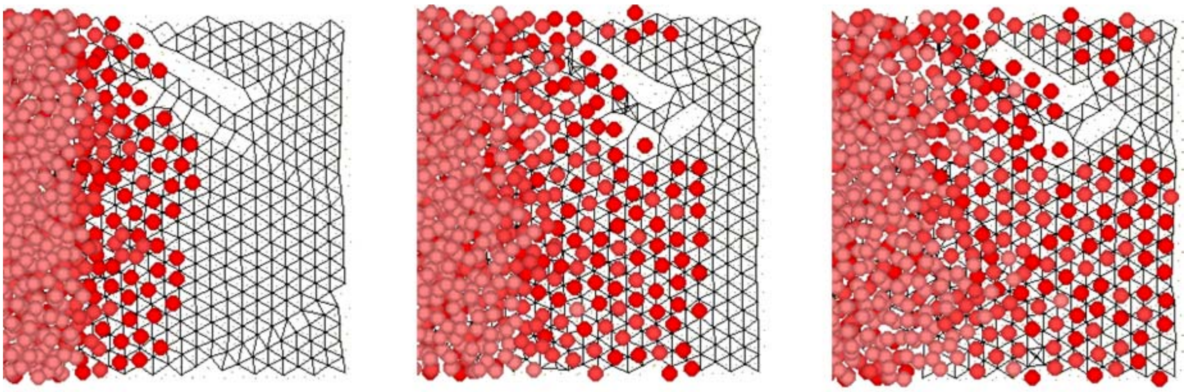
3.3. Thin film structure

Fig. 5 shows snapshots of the wetting front that forms in the In/Cu (111) system, with a viewpoint from a direction perpendicular to the surface; at (a) 40 ps, (b) 88 ps and (c) 128 ps. The lines connect each Cu atom on the surface to show the alignment of the atoms at the



(a) Al/Cu (b) In/Cu (c) Zn/Cu

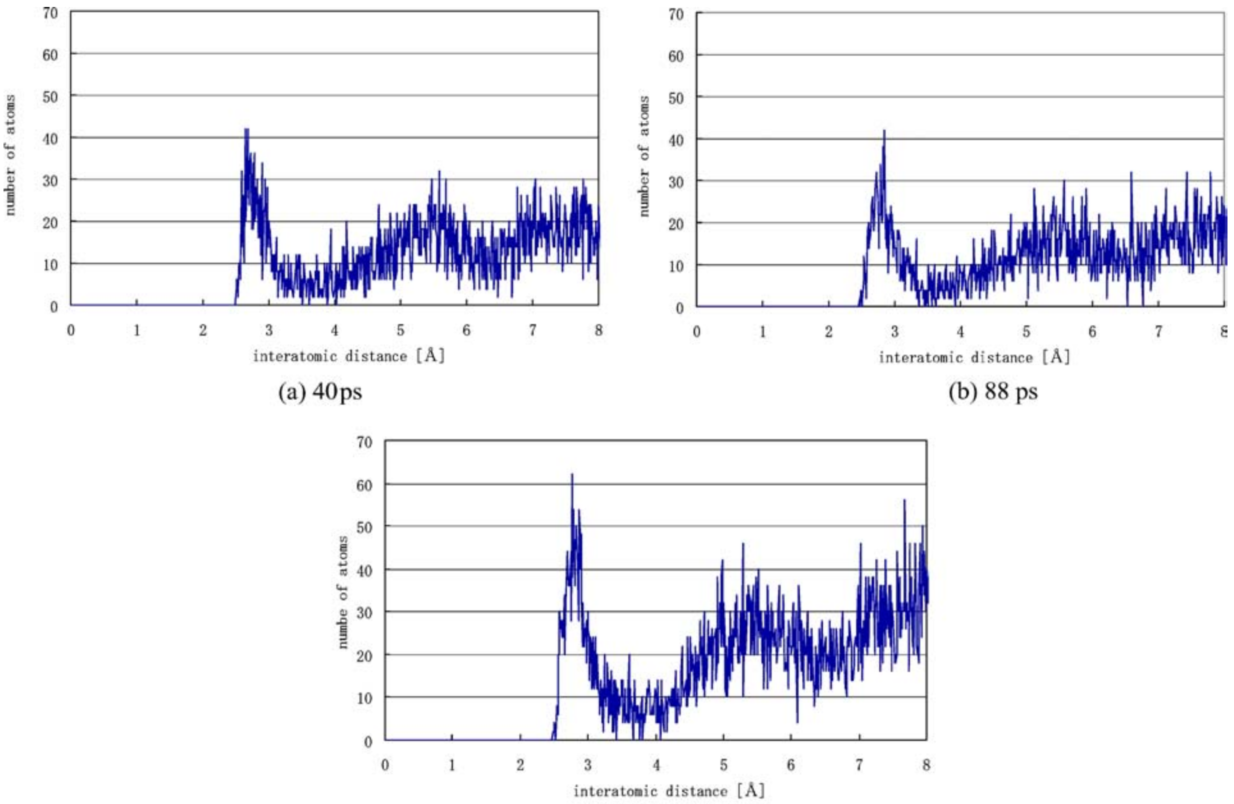
Figure 4 Snapshots of the wetting process of (a) Al/Cu, (b) In/Cu and (c) Zn/Cu on the Cu (111) surface. The wetting on (111) is nonreactive, and a thin film structure (precursor film) can be seen at the wetting front of Al and In atoms.



(a) 40 ps (b) 88 ps (c) 128 ps

Figure 5 Snapshots of the structure of the spreading In/Cu (111) film from a surface perpendicular viewpoint, at (a) 40 ps, (b) 88 ps and (c) 128 ps.

(111) surface. A defectlike structure can be seen in the upper part of the snapshots. These defects were caused by the surface rearrangement when the liquid atoms attach to the surface. The film spread smoothly across a surface having no defects, however, it stopped at the defects of a surface. The atoms that were caught at the defect did not move from there within the simulation time, and the atoms behind these atoms also did not



(a) 40ps (b) 88 ps (c) 128 ps

Figure 6 Radial distribution of In film on Cu (111); simulation times are (a) 40 ps, (b) 88 ps and (c) 128 ps. Peaks became clearer as the simulation time advanced, but the positions of the peaks did not change with simulation time.

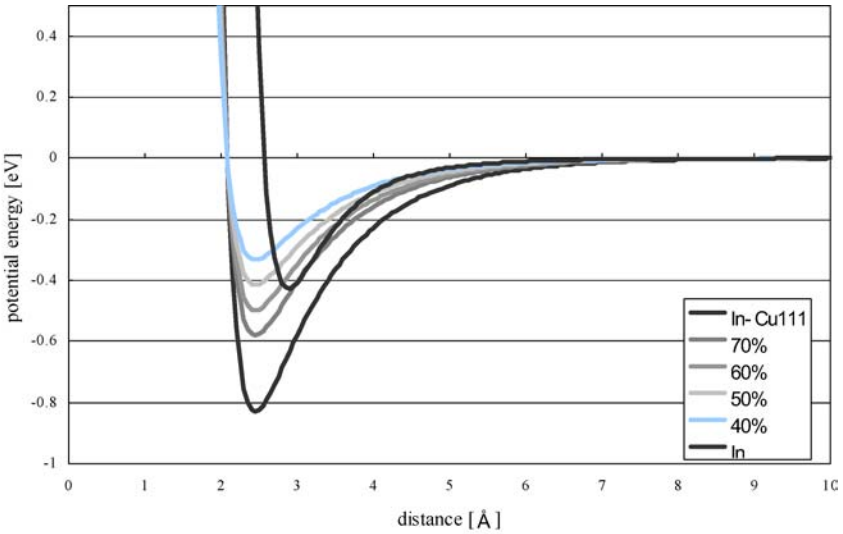
move either. Fig. 6 shows the radial distributions in the lowest layer of the liquid, at (a) 40 ps, (b) 88 ps and (c) 128 ps. The peaks grew with simulation time because the atoms increased on the surface. However, the peak position did not change. This shows that atoms in the film maintain a certain distance from the nearest neighbor atoms.

4. Discussion

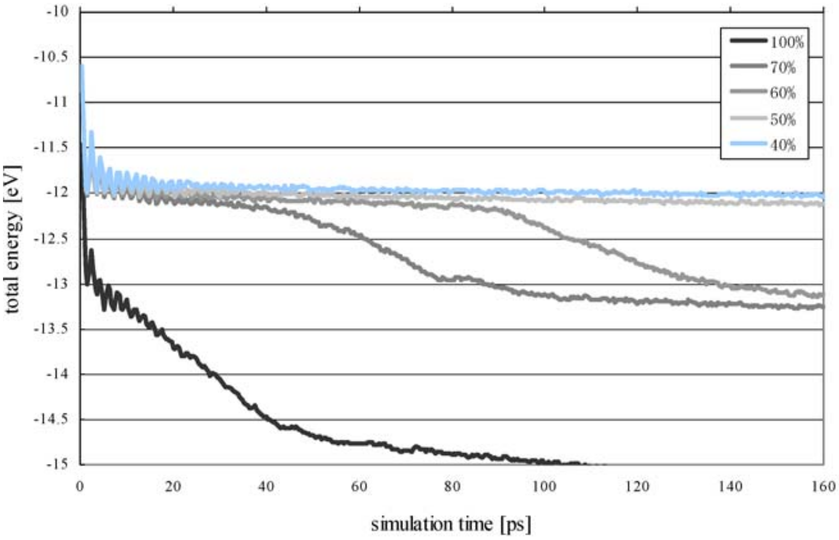
4.1. Wetting behavior

On the basis of Fig. 2, it is suggested that the change of a surface's crystal orientation involves not only a change of the structure but also that of the collective liquid-solid interaction. Comparing the potential depths, the Cu-Cu potentials are (111) > (100) and the (Al, In, Zn)-Cu potentials are (100) > (111). The permutations of the potential depths at each crystal orientation are (100): {In-Cu > Al-Cu > Cu-Cu > Liquids > Zn-Cu} and (111): {Cu-Cu > In-Cu > Al-Cu > Liquids > Zn-Cu}. The potentials are two-body potentials, whose depth represents the interaction strength. The difference in the wetting behavior for different surface orientations is discussed.

In the case of the (100) surface, the interaction relation is Al, In-Cu > Cu-Cu, and therefore Al and In atoms are attracted by the Cu substrate and break the surface structure (reaction). In contrast, the relation on the (111) surface was Cu-Cu > Al, In-Cu, so the liquid atoms cannot break the surface structure (nonreactive wetting). Since the interaction relation of Zn/Cu is Zn-Zn > Zn-Cu, Zn did not spread on either the (100) or (111) surface. Shen *et al.* [12] showed experimentally that the wettability changes with the surface crystal orientation even in the same pair of elements in a number of metal/ceramics systems. The paper concluded that the configuration of the surface atoms influence the wettability. The change seems to be due to the difference not only in the surface structure but also in the collective interaction between the liquid and solid.



(a) Interatomic potential curves of In-Cu (40 to 100%) and In-In



(b) Total energy changes of the systems whose In-Cu interactions are 40 to 100%

Figure 7 Interatomic potential curves and total energy histories of MD calculation in the In/Cu (111) systems whose the strength of the In-Cu interaction are 40, 50, 60 and 70% of the actual potential (100%) fitted to the *ab initio* calculation.

4.2. The characteristics of the precursor film

When we arranged the In atoms in monolayer the dimension of x-y direction is the same as the Fig. 1d and performed MD calculation to clear whether the film spreads or not without droplet, the atoms does not diffuse freely. It means that the film structure can not move in its own. This means that the atoms of the film structure effect each other. From Fig. 6, an influence of the atoms of the film structure appeared the peaks of radial distributions of In film structure which does not change the position independently of the simulation time. From Fig. 5, the forefront part of In liquid film is mainly constructed by the lower layer atoms of the initial state, and the midfield part is constructed by middle layer atoms, and the atom arrangement does not change significantly. This suggests that the liquid atoms are supplied to the film from lower layer of the droplet to turn. The film structure is supplied the liquid atoms at the droplet foot and expands its area. The supplied atoms interrupt between the film structure and the droplet, push aside the atoms of film structure and attach to the Cu substrate. Despite the pushing, the film maintains constant interatomic distance and does not change the density locally.

4.3. The condition for the film formation

Comparing the results of the three systems, it is found that the film structure is formed when the liquid atoms spread well and do not react with the substrate. It appears that the liquid-solid interaction needs a certain amount of strength to form the precursor film.

To clarify the conditions with respect to the interatomic potential, we performed additional calculations to estimate the critical strength of the liquid-solid interaction for the film spreading in the In/Cu (111) system. The calculations are carried out using hypothetical In-Cu interactions whose strengths are 40, 50, 60 and 70% of the actual In-Cu interaction that was fitted to the *ab initio* calculations. (A strength of 50% is almost consistent with that of the In-In interaction.) The potential curves are shown in Fig. 7a. The changes in the total energies of the hypothetical systems with the simulation time are shown in Fig. 7b. The total energy decreases when the precursor film appears because it covers the surface. In Fig. 7b, although the reduction of the total energy is observed in the cases with strength of 60 and 70%, no distinguished reduction is found in the cases with strength of 40 and 50%. It was clarified that a general condition for film formation in the model is that the liquid-solid interaction is stronger than the liquid-liquid interaction.

5. Conclusions

The wetting of Al, In and Zn atoms on the Cu (100) and (111) surfaces were simulated, and the following results were obtained;

1. The interatomic potentials differ with the surface crystal orientation. On the Cu (100) surface, the Cu-Cu interaction is weak compared to the liquid-Cu interactions for Al and In. In contrast, on the Cu (111) surface, the Cu-Cu interaction is stronger than all of the liquid-Cu interactions.
2. Al and In atoms spread well on the Cu substrate. However, the wetting behavior is different for the (111) and (100) surfaces; reactive wetting occurs on the (100) surface and a significantly reduced reaction rate is seen on the (111) surface.
3. The precursor film extends its area by pushing out supplied atoms from droplet, and it has a constant density independent of the simulation time.
4. The precursor film formed when the liquid atoms spread well but do not react rapidly with the substrate. The order of the strength of the model interaction in this case was solid-solid > liquid-solid > liquid-liquid.

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