

On Interatomic Potential Functions for Molecular Dynamic (MD) Simulations of Plasma-Wall Interactions

HAMAGUCHI Satoshi, OHTA Hiroaki and YAMADA Hideaki
Department of Fundamental Energy Science, Kyoto University, Uji 611-0011, Japan
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Abstract

Control of plasma-wall interactions is a key issue in plasma material processing such as reactive ion etching (RIE) and plasma enhanced chemical vapor deposition (PECVD). For magnetic fusion devices, bulk plasma conditions are also often influenced by interactions of the plasma with the first wall and divertor materials. Molecular dynamics (MD) simulations of plasma-wall interactions can give good insight into surface dynamics for plasma-wall interactions. In the light of applications to classical MD simulations, we discuss interatomic potential functions that are designed to describe covalent bonds of surface materials. Reviewing recently developed interatomic potential functions, we examine how such potential models can represent realistic chemical bonds and how the accuracy of employed interatomic potential functions can affect the simulation results.

Keywords:

Molecular Dynamics (MD) simulation, plasma-wall interaction, plasma-surface interaction, plasma processing, reactive ion etching

1. Introduction

Plasma processes such as reactive ion etching (RIE) and plasma enhanced chemical vapor deposition (PECVD) constitute a large and essential part of semiconductor manufacturing processes today [1,2]. For such applications as well as other industrial applications of plasmas, controlling plasma-wall (*i.e.*, plasma-surface) interactions is of significant importance since the quality of processed materials is largely determined by such interactions. For magnetic fusion devices, too, study of plasma-wall interactions has attracted much attention of the research community as the bulk plasma conditions are often influenced by interactions of the plasma with the first wall and divertor materials.

Recently various investigators have examined surface reaction mechanisms for materials exposed to beams or plasmas by using molecular dynamics (MD) simulations [3-9]. It has been demonstrated that such MD simulations can provide useful, and sometimes quantitatively reliable, information on plasma-surface interaction.

For classical MD simulations, reliability of their results is in general largely affected by the choice of interatomic potential functions for the particles constituting the system. To simulate plasma-surface interaction, one usually needs to handle a large number of particles (*i.e.*, atoms) and repeat similar simulation runs for sufficiently many times to reduce statistical noise, the simulation cost of which precludes the use of more detailed *ab initio* (*i.e.*, quantum mechanical)

simulations. Therefore in MD simulations the employed potential model needs to be sufficiently representative of the true atomic interactions for the system. In this article, we review recently developed interatomic potential functions and examine how such potential models can represent realistic chemical bonds and how the accuracy of employed interatomic potential functions can affect the simulation results.

2. Potential functions for covalent bonds

When several atoms are interacting, the force exerted on each atom may be regarded as a multi-body force in the time scale of atomic motion since electron orbitals are often shared by multiple atoms. If there are N atoms and the position of the i th atom is given by \mathbf{r}_i , then the total potential energy of the system V may be written in cluster expansion as

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i < j} v_{ij}^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} v_{ijk}^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots + v_{12\dots N}^{(N)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (1)$$

Here $v_{ij}^{(2)}$ is called the two-body potential, $v_{ijk}^{(3)}$ the three-body potential, and so on. The functions also depend on atomic species denoted by the subscripts. This expansion can be done uniquely, regardless of the nature of atomic interactions. For

example, interactions of rare gas atoms may be well approximated by the first term only, possibly by the well-known Lennard-Jones potential. In general, for given atoms, it is nearly impossible to construct classical interatomic potential functions with high accuracy in the form of eq. (1) since it is hardly practical to take into account all possible multi-body interactions. Therefore, depending on the purpose of simulations, we selectively incorporate only the important effects of atomic interactions and represent them by relatively simple functional forms, so that we can achieve both computational efficiency of classical MD simulations and reasonable accuracy of atomic dynamics.

Stillinger and Weber [3] suggested that the total potential energy of the system may be written as

$$\Phi = \sum_{i < j} v_2(i, j) + \sum_{i < j < k} v_3(i, j, k) \quad (2)$$

with $v_2(i, j) = v_{ij}^{(2)}(\mathbf{r}_i, \mathbf{r}_j)$ being the pair interaction:

$$v_2(i, j) = \left[\frac{A_{ij}}{r_{ij}^{p_{ij}}} \exp\left(\frac{C_{ij}}{r_{ij} - a_{ij}}\right) - \frac{B_{ij}}{r_{ij}^{q_{ij}}} \exp\left(\frac{D_{ij}}{r_{ij} - a_{ij}}\right) \right] \quad (3)$$

if $r_{ij} < a_{ij}$ and $v_2(i, j) = 0$ otherwise. Here $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the distance between the i th and j th atoms located at \mathbf{r}_i and \mathbf{r}_j . The parameters, A_{ij} , B_{ij} , C_{ij} , D_{ij} , p_{ij} , q_{ij} and a_{ij} depend only on the element types (such as silicon or oxygen) of the i th and j th atoms.

The three-body term

$$v_3(i, j, k) = v_{ijk}^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

in eq. (2) may be written as

$$v_3(i, j, k) = h_{jik}(r_{ij}, r_{ik}, \theta_{jik}) + h_{ijk}(r_{ji}, r_{jk}, \theta_{ijk}) + h_{ikj}(r_{ki}, r_{kj}, \theta_{ikj}) \quad (4)$$

with θ_{jik} being the angle spanned by vectors $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_{ik} \equiv \mathbf{r}_k - \mathbf{r}_i$ at vertex \mathbf{r}_i . The commonly used functional form [3] for h_{jik} is given by

$$h_{jik}(r, s, \theta) = \left(\lambda_{jik} |\cos \theta - \cos \theta_{jik}^0|^{2\alpha_{jik}} + \mu_{jik} \right) \times \exp\left(\frac{\gamma_{jik}^j}{r - a_{jik}^j} + \frac{\gamma_{jik}^k}{s - a_{jik}^k} \right) \quad (5)$$

if $r < a_{jik}^j$ and $s < a_{jik}^k$. Otherwise $h_{jik} = 0$. Here, λ_{jik} , μ_{jik} , γ_{jik}^j , γ_{jik}^k , a_{jik}^j , a_{jik}^k , θ_{jik}^0 , and α_{jik} are parameters that depends only on the element types of the i th, j th, and k th atoms. Here the original Stillinger-Weber (SW) functional form is modified slightly by introducing a new parameter α_{jik} in order to improve parameter fitting. As can be seen from the functional form with λ_{jik} being non negative ($\lambda_{jik} \geq 0$), the three-body potential above is designed to penalize the system if atoms are not configured to form the most stable molecules. For example, the potential parameters for the Si-F-O (*i.e.*, a

system consisting of Si, F, and O atoms) and Si-Cl-O systems are found in ref. [5].

We note that the concept of ‘‘covalent bonds’’ are not directly incorporated in the SW potential. However, the three-body potential h_{ijk} works to help atoms form effective bonds. To see this, it is instructive to consider the exchange reaction



where a single H atom is assumed to approach a hydrogen molecule H_2 in the direction of its bond axis. The parameters for the SW potential for hydrogen are given in Table 1, which we obtained by fitting the functions to *ab initio* data. [6] Figures 1 and 2 show the potential energy of the system. As shown in Fig. 2, r_{12} and r_{23} denote the distances between the H atoms. In Fig. 1 filled points represents potential energies obtained from *ab initio* quantum mechanical calculations and the solid lines denotes the corresponding values of the SW potential model.

It is shown in Fig. 1 that, as a single H atom approaches the H_2 molecule, *i.e.*, r_{23} decreases, the potential well seen in Fig. 1(a) disappears. This indicates that no bond is formed between H and H_2 and the atoms of H_2 are tightly bound to each other until the distance between H and H_2 reaches about 1 Å or less. As can be seen in Figs. 1(c), if the three H atoms are sufficiently close, no attractive force is present. The potential energy profile as a function of r_{12} and r_{23} , given by the obtained SW potential, is shown in Fig. 2. This figure demonstrates the formation of bonds is incorporated in the SW potential and it is controlled by the three-body potential.

There is another class of potential functions that directly take into account the formation of covalent bonds. Based on the general expression for bond energies derived by Abell [10], Tersoff proposed a functional form of covalent bonds [11]. The basic idea of this potential (which we call Abell-Tersoff potential or AT potential in short) is first to identify bonds among atoms and then to have the strength of each bond depend on the positions of surrounding atoms. Under these assumptions, the total potential energy of the system may be given by

$$V = \sum_{i < j} [V_{ij}^R(r_{ij}) - B_{ij} V_{ij}^A(r_{ij})] \quad (7)$$

Table 1 Parameters of the SW potential functions, *i.e.*, eqs. (3), (4) and (5), for hydrogen atoms. Units of energy and length are eV and Å. Units of parameters are selected accordingly.

| 2 body parameters | | 3 body parameters | |
|-------------------|--------|-------------------|--------|
| A_{HH} | 7.709 | λ_{HHH} | 0 |
| B_{HH} | 16.747 | μ_{HHH} | 353.15 |
| C_{HH} | 0.7398 | γ_{HHH} | 3.433 |
| D_{HH} | 0.7663 | α_{HHH} | 1.0 |
| p_{HH} | 1.914 | a_{HHH} | 2.488 |
| q_{HH} | 1.035 | | |
| a_{HH} | 2.0 | | |

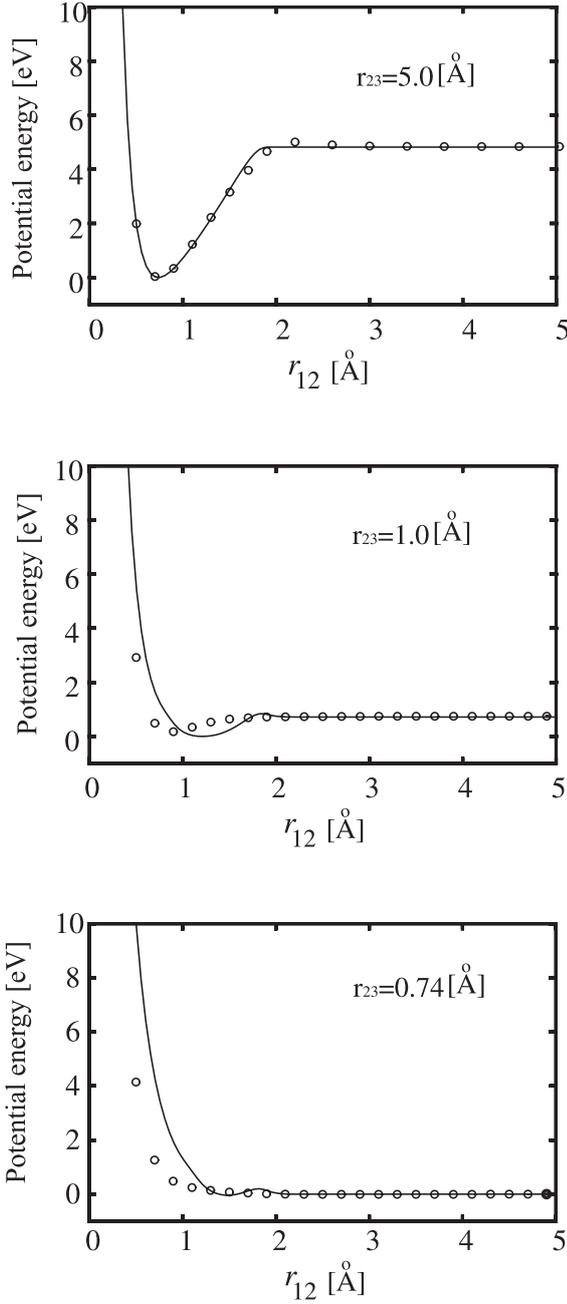


Fig. 1 The potential energy of three linearly aligned H atoms H-H-H. The distances between the first and second, and second and third H atoms are denoted by r_{12} and r_{23} . Symbol \diamond denotes data points obtained from *ab initio* quantum mechanical calculations and the solid lines are the values of eqs. (3), (4) and (5) with parameters given in Table 1. The zero energy level is set to be the bottom of the potential well, *i.e.*, the potential energy for the most stable state of H_2 molecule.

where V_{ij}^R denotes the repulsive potential and V_{ij}^A denotes the attractive potential. Effects of multi-body interactions are included in coefficient B_{ij} . Coefficient B_{ij} typically depends on the numbers of atoms surrounding the atom at each end of the bond (*i.e.*, coordination number) and the angles formed by the bond and neighboring atoms. Morse potentials [$\propto \exp(-\beta r)$] are usually used for functions V_{ij}^R and V_{ij}^A . Examples of the AT potential for the C/H system are found in ref. [12].

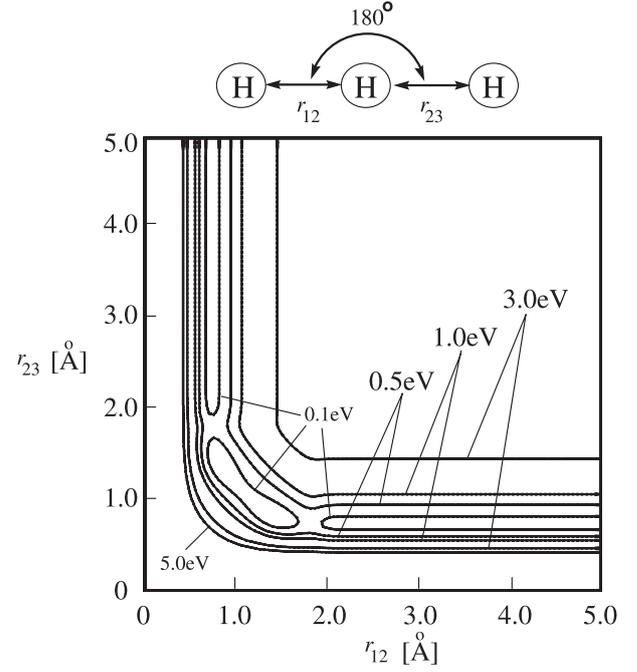


Fig. 2 The potential energy of three linearly aligned H atoms given by the SW potential. Bond formation of the closest two H atoms is shown to be reproduced by the SW type potential due to the three-body interaction term.

One can also combine the SW potential with the AT potential by making the SW potential functions depend explicitly on the conditions of surrounding atoms. For example, one may write the total potential energy as

$$\Phi = \sum_{i < j} v_2(i, j; g_{ij}) + \sum_{i, j, k} h_{i, j, k}(r_{ij}, r_{jk}, \theta_{ijk}; g_{ij}, g_{jk}), \quad (8)$$

where g_{ij} represents the bond order of the possible bond between the i th and j th atoms. ($g_{ij} = 0$ if there is no covalent bond between the i th and j th atoms.) This factor is typically a function of the coordination numbers or more generally a function of the positions of surrounding atoms. The idea is to use the two-body and three-body potentials only for the pair $(\mathbf{r}_i, \mathbf{r}_j)$ that forms a covalent bond.

We note that the bond order g_{ij} can be determined by how the valence electrons of the atom at each end of the bond are shared with neighboring atoms. For examples a carbon atom has four valence electrons that may be shared with neighboring atoms. In the neighborhood of this carbon atom, if there are more than four atoms (*e.g.*, 5 H atoms) that can share the electrons with this C, the same (excessive) number of bonds (*e.g.*, 5 C-H bonds) may be formed but the strength of each bond is reduced accordingly. On the other hand, for example, if there are fewer than four carbon atoms in the neighborhood of a carbon atom, some of the valence electrons may be used to form π bonds, resulting in double or triple bonds between carbon atoms.

Once the dependence on g_{ij} is introduced in the two-body term, the separation of the three-body term h_{ijk} of eq. (8) from the total potential energy becomes somewhat arbitrary since

some of the three-body (and higher-order) effects are then already included in g_{ij} . In the case of the AT potential, the bond-angle [*i.e.*, θ_{ijk} in eq. (5)] dependence [12] is usually incorporated in coefficient of B_{ij} eq. (7) whereas, in the case of eq. (8), the bond-angle dependence is left in the “three-body” term h_{ijk} .

So far we have discussed potential functions that represents only covalent bonds. Other interatomic interactions such as Van der Waals (VW) interactions and Coulomb interactions can also play important roles. For example, the importance of VW interactions is discussed in a companion paper ref. [9].

3. Discussion

Using potential functions similar to eq. (8) we have developed covalent-bond potential functions for Si/O/F/C systems [9] and C/N/H systems [6]. Using these model potentials together with appropriate VW interaction potentials, we have applied MD simulations to study plasma etching and deposition processes. An example of such simulation results is given in Figure 3, which shows sputtering yields for SiO₂ etching by F or fluorocarbon (*i.e.*, CF_x with $x = 1, 2, 3$) beams. In general, sputtering yields depend on injection dose and the results shown in Fig. 3 are those with very low injection doses. Experimentally it is known that, for example, a CF beam into a SiO₂ substrate causes etching for a very short initial time period and then results in deposition of fluorocarbon films on the substrate in this energy range. Such experimental observation is consistent with our MD simulation results given in Fig. 3 although we have not been able to make quantitative comparison of sputtering yields between MD simulations and beam experiments yet. Our recent results based on longer simulation runs indeed indicate the process turns from etching to deposition as the accumulation of

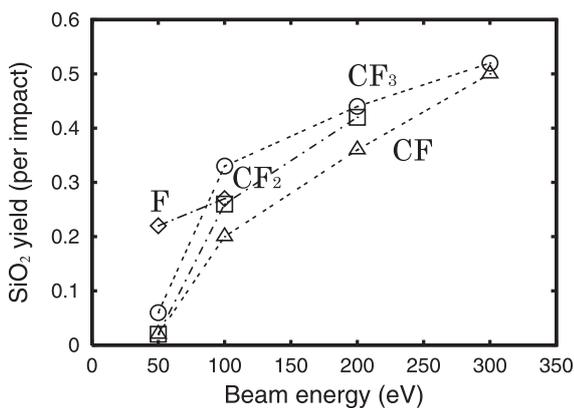


Fig. 3 Sputtering yields of SiO₂ by CF_x ($x = 1, 2, 3$) and F beams as functions of injection energy, obtained from MD simulations. The yield generally depends on the injection dose as well. The data presented here are yields when injection doses are very low. Van der Waals interactions are not taken into account in these simulations.

carbon atoms in the substrate material becomes significantly large. Some details of these simulations may be found in ref. [9] and the rest will be published elsewhere. We have also performed MD simulations of an organic polymer, details of which may be found in refs. [7,8].

To summarize, we have discussed interatomic potential functions that are used in MD simulations for plasma (or beam)-surface interactions. The AT potential is especially design to incorporate covalent bond structures but, as demonstrated in Fig. 2, the SW potentials can also model bond formation with good accuracy if the three-body potential is appropriately chosen. We can also extend the SW potentials to explicitly incorporate bond structures as given in eq. (8). For MD simulations of plasma-surface interactions, where kinetic energies of impinging species are much higher than interatomic bond energies, physical quantities such as etch rates, deposition rates, etch product species, *etc.*, may not depend sensitively on details of interatomic potential functions. From various MD simulations that have been performed to date, it seems these macroscopic quantities are most sensitively depend on bond energies and bond lengths given by the interatomic potentials. To confirm this, however, one would need further analyses on the dependence of such macroscopic data on the potential functions.

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