S4-2 Molecular Dynamics Simulation of Chemical Sputtering
MD シミュレーションによる化学スパッタリングの物理機構解析

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Surface sputtering processes by plasmas often involve surface chemical reactions. The physical mechanisms of such chemical sputtering processes, which are also known as reactive ion etching (RIE) processes, are not yet completely understood. In the present work we shall present the method of molecular dynamics (MD) simulation to analyze chemical reactions occurring on a material surface which is subject to simultaneous energetic ion bombardment and the inflow of charge- neutral radical species. Especially our recent analyses of carbon-based material etching processes by hydrogen or hydrocarbon plasmas are reviewed.

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 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. It has been demonstrated that such MD simulations can provide useful, and sometimes quantitatively reliable, information on plasma-surface interactions.

For classical MD simulations, reliability of the 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 of energetic particle injections for sufficiently many times to reduce statistical noise. Therefore, the cost of such simulations precludes the use of more detailed *ab initio* (i.e., quantum mechanical) simulations. In classical MD simulations, therefore, the employed potential model needs to be sufficiently representative of the true atomic interactions for the system.

In this work, we shall review the method of MD simulation to analyze chemical sputtering processes, i.e., chemical reactions occurring on a material surface which is subject to simultaneous energetic ion bombardment and the inflow of charge- neutral radical species, using examples of our recent analyses of carbon-based material etching processes by hydrogen or hydrocarbon plasmas.

2. Interatomic potential functions for covalent bonds

First let us briefly discuss the classical interatomic potential functions. 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

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

In this way, 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. In Eq. (1), $v_{ij}^{(2)}$ is called the two-body potential, $v_{ijk}^{(3)}$ the three-body potential, and so on. 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 classical MD simulations and reasonable accuracy of atomic dynamics [3].

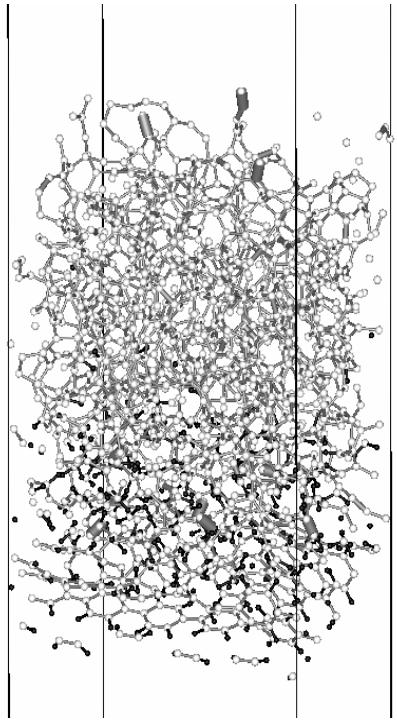

Fig.1: Surface morphology of PPP after 2.4×10^{16} atoms/cm^2 dose of carbon atom injections. White and black spheres represent carbon and hydrogen atoms

3. MD simulations

In MD simulations, the equations of motion based on the interatomic potentials mentioned above are solved numerically [3-8]. The substrate material is placed in a simulation cell and periodic boundary conditions are imposed in the horizontal directions. Physical quantities such as sputtering yields generally depend on beam dose and usually are measured after the surface conditions reach a steady state by sufficient beam bombardment. Energetic particles (e.g., atoms, molecules, radicals, etc.) are injected from randomly chosen locations to the surface with a given injection angle. Most transient etching processes such as breaking and re-formation of bonds by particle bombardment typically occur within a pico second. Therefore each ion bombardment may be considered as an independent process. To simulate a series of such independent processes efficiently, we usually solve the motions of all particles under constant-energy conditions for a certain time interval (typically of the order of pico seconds) after each injection and then apply artificial cooling to the system in a relatively short period (again typically of the order of pico seconds). At the end of this cooling process, a new energetic particle is directed to the surface and the whole simulation cycle is repeated.

Chemical sputtering processes of the surface often proceed simultaneously with deposition processes of some specific atomic/molecular species. Deposition processes are in general more sensitive to the thermal relaxation processes, so one needs to incorporate thermal effects in MD simulations effectively. One possibility for such processes is to use a Monte Carlo algorithm. In the presentation, we review the recent development of MD simulation methods to study beam/plasma-surface interactions, using our recent results of sputtering/deposition processes for carbon-based materials by hydrogen or hydrocarbon plasmas [6,7].

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