Molecular Dynamics and Density Functional Simulations of Tungsten Nanostructure Formation by Helium Plasma Irradiation

A. M. Ito¹, A. Takayama¹, Y. Oda¹, T. Tamura², R. Kobayashi², T. Hattori², S. Ogata², N. Ohno³, S. Kajita³, M. Yajima³, Y. Noiri³, Y. Yoshimoto⁴, S. Saito⁵, S. Takamura⁶, T. Murashima⁷, M. Miyamoto⁸, and H. Nakamura¹,³

¹National Institute for Fusion Science, 322-6, Oroshi-cho, Toki 509-5292, Japan.
²Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.
³Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.
⁴University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
⁵Kushiro National College of Technology, Kushiro, Hokkaido 084-0916, Japan.
⁶Aichi Institute of Technology, 1247 Yachigusa, Yakusa-cho, Toyota 470-0392, Japan.
⁷Tohoku University, 6-3, Aramaki-Aza-Aoba, Aoba-Ward, Sendai 980-8578, Japan.
⁸Shimane University, Matsue, Shimane 690-8504, Japan.

E-mail contact of main author: ito.atsumi@nifs.ac.jp

Abstract. For the purposes of long-term use of tungsten diverter walls, it is necessary to suppress the surface deterioration due to the helium ash which induces the formations of helium bubbles and tungsten fuzzy nanostructures. In the present paper, the formation mechanisms of helium bubbles and tungsten fuzzy nanostructures were explained by the four-step process which is composed of the penetration process, the diffusion and agglomeration process, the helium bubble growth process and the tungsten fuzzy nanostructure formation process. The first to third step processes of the four-step process were investigated by using binary collision approximation, density functional theory and molecular dynamics, respectively. Furthermore, newly developed molecular dynamics and Monte-Carlo hybrid simulation has successfully reproduced the early formation process of tungsten fuzzy nanostructure. From these simulations, we here suggest the following key mechanisms of the formations of helium bubbles and tungsten fuzzy nanostructures: (1) By comparison between helium, neon, argon and hydrogen, the noble gas atoms can agglomerate limitlessly not only at a vacancy but also at an interstitial site. In particular, at the low incident energy, only helium atoms bring about the nucleation for helium bubble. (2) In the helium bubble growth process, the strain of the tungsten material around a helium atom is released as a dislocation loop, which is regarded as the loop punching phenomenon. (3) In the tungsten nanostructure formation process, the bursting of a helium bubble forms cavity and convexity in the surface. The helium bubbles tend to be grown and to burst at the cavity region, and then the difference of height between the cavity and convexity on the surface are enhanced. Consequently, the tungsten fuzzy nanostructure is formed.

1. Introduction

The phenomenon that tungsten fuzzy nanostructure is generated by helium plasma irradiation was found from experimental researches [1] on plasma-wall interaction for nuclear fusion reactors. If the tungsten fuzzy nanostructure is generated on the tungsten divertor plates by the exposure to helium ash, it is concerned about the decrease of the maximum allowable heat
load and the erosion by arcing on the surface of the tungsten fuzzy nanostructure. To suppress the generation of the tungsten fuzzy nanostructure, the formation mechanisms of the tungsten fuzzy nanostructure should be understood. For this purpose, we had researched on the tungsten nanostructure formation by using molecular dynamics (MD), density functional theory (DFT) and binary collision approximation (BCA) and Monte-Carlo (MC) simulations.

In the present paper, we propose a four-step process to explain the formation mechanisms of helium bubbles and tungsten fuzzy nanostructures. The formation process is classified into penetration process, diffusion and agglomeration process, helium bubble growth process, and tungsten fuzzy nanostructure formation process. The first to third step processes of the four-step process are analyzed by using BCA, DFT and MD, respectively.

For the fourth step process of the four-step process, furthermore, we developed the new hybrid simulation approach in which MD and MC simulations are combined to reproduce the formation process of the tungsten fuzzy nanostructure.

2. Four Step Process of Tungsten Fuzzy Nanostructure Formation

The formation process of the tungsten fuzzy nanostructure is the problems of multi-scale and multi-physics of helium-tungsten interaction. Major phenomena in the tungsten material bombarded by helium plasma are shown in FIG. 1. To clarify the formation mechanism of the tungsten fuzzy nanostructure, we propose a four-step process for the formation of helium bubbles and tungsten fuzzy nanostructures. The four-step process is composed of the penetration process, the diffusion and agglomeration process, the helium bubble growth process, and the tungsten fuzzy nanostructure formation process.

2.1. The First Step: Penetration Process

The first step is the penetration process of irradiated helium ions into tungsten surfaces. In particular, the competition between the penetration of helium atoms and the sputtering of tungsten surfaces is important factor. To clarify penetration process, we evaluated the energy range for of helium, neon, argon and hydrogen atoms were evaluated.

The upper limit of the energy range for penetration is defined as the sputtering threshold

![Diagram](FIG. 1. The multi-scale multi-physics phenomena of formations of helium bubbles and tungsten fuzzy nanostructures, which is classified into the four-step process.)
The sputtering threshold energy $E_{sp}$ can be calculated by the BCA with the AC\textsuperscript{\scriptsize $\mathbf{T}$} code (see TABLE I)[2]. The lower limit of the energy range for penetration is defined as the barrier energy on the incident path from vacuum into a surface. Assuming that the difference between the barrier energy and the solution energy, which is energy difference between vacuum and an interstitial site, is small, the solution energies were calculated by the DFT with the QMAS code[3] (see TABLE I)[4]. The solution energy of a helium atom, 6.29 eV, agrees with the experimental measured lower limit to generate helium bubbles, 6.0 eV[5,6]. From these calculations, it is understood that the energy ranges for helium and hydrogen penetration are wide, while the energy ranges for neon and argon penetration are narrow.

In addition, the penetration depths of irradiated atoms were calculated. Maximum penetration depth is the penetration depths in the case that incident energies are the upper limits of penetration. Maximum penetration depths calculated by BCA are shown in TABLE I. The maximum penetration depth of neon and argon atoms are corresponding to only monolayer of body centered cubic lattice structure of tungsten material. This fact expects that penetrated neon and argon promptly escape from the tungsten surface.

### 2.2. The Second Step: Diffusion and Agglomeration Process

The second step is the diffusion and agglomeration process of helium atoms in tungsten material. In this step also, helium is compared with neon, argon and hydrogen.

First, to confirmed the possibility of helium agglomeration, the binding energies at a mono-vacancy and an interstitial site were calculated by DFT with the OpenMX code[7]. The binding energies at a mono-vacancy of helium, neon, argon and hydrogen atoms are shown in FIG. 2[8,9]. From this figure, it is understood that the binding energy for hydrogen atoms becomes almost 0.0 eV or negative at the case of the cluster of 7 atoms, which is in agreement with the calculation by Kato et al.[10] and Ohsawa et al.[11]. On the other hand, the binding energies of noble gas atoms are positive always positive at least the cluster composed of 15 atoms. This fact expects that although the agglomeration of hydrogen atoms is limited, the agglomeration of helium, neon and argon atoms are unlimited.

Further, the DFT disclosed that helium, neon and argon can agglomerate also at interstitial site in tungsten materials[4,12-14]. From the DFT, the binding energy at interstitial site increases from 1.0 eV to 2.5 eV as the number of helium atoms clustering at interstitial site increases.

Next, the diffusion process of the helium, neon, argon and hydrogen atoms was researched. The migration paths of helium, neon, argon and hydrogen atoms are common path from a tetra-site to the next tetra-site. To compare the speed of diffusion, migration energies were

### TABLE I: THE SOLUTION ENERGY $E_{sol}$, THE SPUTTERING THRESHOLD ENERGY $E_{sp}$, THE PENETRATION DEPTH $D_{pen}$, THE MIGRATION BARRIER ENERGY $E_{mig}$

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_{sol}$ [eV]</th>
<th>$E_{sp}$ [eV]</th>
<th>$D_{pen}$ [Å]</th>
<th>$E_{mig}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>6.29</td>
<td>100</td>
<td>100</td>
<td>0.06</td>
</tr>
<tr>
<td>Neon</td>
<td>11.55</td>
<td>30</td>
<td>6</td>
<td>0.17</td>
</tr>
<tr>
<td>Argon</td>
<td>14.99</td>
<td>20</td>
<td>4</td>
<td>0.19</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-2.47</td>
<td>700</td>
<td>1000</td>
<td>0.20</td>
</tr>
</tbody>
</table>
calculated by DFT as shown in TABLE I[4]. As a result, the migration barrier energy of helium is one-third of that of hydrogen. From these facts, we suggest that helium diffuses faster than hydrogen in tungsten material. In addition, although they have larger atomic radius, the migration barrier energies of neon and argon were similar to that of hydrogen.

More interestingly, a recent work by the DFT revealed that the migration energy of helium dimer, which is clustering at interstitial site, is lower than that of the single helium atom[15]. Moreover, Zhou et al.[16] also reported that the diffusion coefficient of helium dimer is larger than the diffusion coefficient of a helium atom from MD simulation.

By comparison between helium, neon, argon and hydrogen in the penetration process and the diffusion and agglomeration process, the possibility of bubble formation of helium is the largest in these atomic elements. Neon and argon atoms have narrow energy range for penetration, while hydrogen atoms cannot agglomerate in a tungsten material. The penetration depths of neon and argon are too shallow to be retained. The reason why bubble structures were not generated by neon and argon irradiation with the incident energy of less than sputtering threshold energy in our previous experiment with NAGDIS-II [17] is that the retention amounts of neon and argon atoms did not reach sufficient amount to generate bubbles. Actually, the bubble structures under the higher energy irradiation of neon and argon with the incident energy of keV scale was confirmed in experiments[18].

2.3. The Third Step: Helium Bubble Growth Process

The third step is helium bubble growth process. Here, a helium cluster of 1 nm or greater in diameter is regarded as the helium bubble. In this step, the growth of helium bubbles was simulated by MD with GLIPS code because the space and time scales of helium bubble are too large to calculate by DFT. The potential model for helium-tungsten system[19] was developed by using the downfolding method[20], which can optimize potential function by comparison with structure and energy data calculated by DFT.

The snapshot with the time evolution in the MD is shown in FIG. 3. It is understood the helium atoms form clusters and then the clusters grow to the helium bubbles of 1nm or greater in diameter. In the present MD simulation, we tried the two conditions in which the vacancies of 5 percent to tungsten atoms were initially prepared in the simulation system or not. Consequently, the generation of helium bubble was confirmed in the both cases with/without the initial vacancies. Namely, not only the agglomeration of helium atoms at the vacancy but also the agglomerate of helium atoms at interstitial site, which were predicted in the second step, induce the nucleation of the helium bubble.
Moreover, the phenomenon called loop-punching was observed in our MD simulation. Although the MD observation of the loop-punching had been reported by Sefta, et al. [21], our MD observation [22] explicitly revealed that the phenomenon of loop-punching is the release of dislocation loops from the helium bubbles as follows: As the size of a helium bubble increases, the strain on tungsten atoms around the helium bubble increases. The strain on tungsten atoms is released as a dislocation loop. The dislocation loop moves along the <111> direction in a tungsten material. When the dislocation loop stops, the region around the dislocation loop becomes a new nucleation site of helium bubbles.

2.4. The Fourth Step: Fuzzy Nanostructure Formation Process

To reproduce the fuzzy nanostructure formation is difficult if we adopt either MD or MC simulation. In the present work, we develop the hybrid simulation between MD and MC, where we call the MD-MC hybrid simulation [9].

In the MD-MC hybrid simulation, the diffusion process of injected helium atoms, which is a long time scale phenomenon, is simulated by MC, and the deformation of tungsten materials and helium bubbles, which should be represented by realistic atomic interactions, is simulated by MD. In each MC process, the injected helium moves as a random walk on a discrete cell which is generated from the atomic configuration just after the previous MD process. The stop position of the random walk in the MC process is taken over as the position of doping helium atoms in the next MD process. In each MD process, the doping helium atoms are initially added into the tetra site in the region of the cell of the stop position. After that, the equations of motions of atoms are solved similarly to general MD simulation.

Time evolution in the MD-MC hybrid simulation is shown in FIG. 4. The observed formation process of the fuzzy nanostructure is as follows: Helium atoms formed helium bubbles. The MD-MC hybrid simulation cannot evaluate elapsed time because the MC and MD phase have different time scales. Here, we should use the fluence of helium instead of elapsed time. As the fluence of helium increases, the size of helium bubbles increases. Because a helium bubble pushed up a tungsten surface, the tungsten surface forms an arch structure on the helium bubble. When the helium bubble bursts, the break point of the arch structure is the supporting point of arch, and is not arch crown part. The arch structure is turned up by helium atoms escaping from the helium bubble. Thus, by the bursting of a helium bubble, the turned-up region in the arch structure changes into convexity, and the region of the helium bubble changes into concavity.

The bursting of the helium bubble occurs one after another. From the simulation result, the helium bubble tends to be generated in the region of concavity rather than convexity.
The cavity region was dig up more and more by the bursting, while the convexity region was lifted up by the helium bubble grown under its region. Thus, the difference of height between cavity and convexity on the surface is enhanced. Thus, the repetition of the bursting generates the tungsten fuzzy nanostructure.

Here, let us discuss the time scale of the fuzzy nanostructure formation in the MD-MC hybrid simulation. The elapsed time in the MD-MC hybrid simulation cannot be evaluated because the MD process and the MC process have the different time scale. Therefore, instead of the elapsed time, the fluence of helium atoms is employed to compare the time scale of the formation process of the tungsten fuzzy nanostructure. In experiments, generally, the fluence of helium atoms for $10^{24}-10^{25}$ m$^{-2}$ is required to generate the tungsten fuzzy nanostructure[23]. However, the fluence of the present MD-MC hybrid simulation is only up to $4.8 \times 10^{21}$ m$^{-2}$. This hundreds to thousands of gap in the fluence of helium atoms is explained by the two effects which were not treated in the MD-MC hybrid simulation. One is the reflection process of irradiated helium atoms on a tungsten surface. The reflection ratio of the irradiated helium atoms estimated by BCA calculation is 20 percent or more. The other is the difference of the retention amount of helium atoms in the diffusion process. The experimental measurement by Lee et al.[24] and the kinetic Monte-Carlo (KMC) simulation evaluated that the retention ratio of helium atoms is 2.0 percent or less. Consequently, the differences of reflection and retention of helium atoms can explain several hundreds of gap in the fluence between experiments and the present MD-MC hybrid simulation. In addition, the formation process of the tungsten fuzzy nanostructure reproduced by the present MD-MC hybrid simulation is early process. To generate larger structure observed by experiments, the MD-MC hybrid simulation probably needs ten times as much as the fluence of helium atoms.

Surface structure generated by the MD-MC hybrid simulation should be scientifically compared with the tungsten fuzzy nanostructure observed by experiments. We are planning to compare the fractal dimension of surface structure. We had already measured the fractal dimension of the tungsten fuzzy nanostructure by the experiment[25]. Experimental fractal dimension was 2.2 to 2.6.

Strictly speaking, the present MD-MC hybrid simulation has the problem that the one side of the simulation box perpendicular to the cross section shown in FIG. 4 is thin. We have tackled a larger scale MD-MC hybrid simulation with thick simulation box. Then, we will be able to evaluate the fractal dimension in near future.
3. Conclusion

In the present paper, the formation processes of helium bubbles and tungsten fuzzy nanostructures were explained by the four-step process. Several simulation methods should be selected step by step.

In the first process of the four-step process, which is the penetration process, the BCA and DFT showed that the incident energy ranges for penetration of helium and hydrogen are wider than that of neon and argon. In the second process of the four-step process, which is the diffusion and agglomeration process, the DFT showed that helium atoms can agglomerate limitlessly not only at a mono-vacancy but also at an interstitial site, and the diffusion of helium is faster than hydrogen, neon and argon. In the third process of the four-step process, which is the helium bubble growth process, the MD showed that helium clusters agglomerated at the both of a mono-vacancy and interstitial sites grew into the helium bubble of 1 nm or greater in diameter. In addition, the MD revealed the natural shape of a phenomenon called the loop punching as the release of a dislocation loop from strained tungsten atoms around a helium bubble.

For the fourth process of the four-step process, the early formation process of the tungsten fuzzy nanostructure was successfully reproduced by the MD-MC hybrid simulation. From the simulation result, the formation process of the tungsten fuzzy nanostructure was revealed as follows: The surface region of tungsten material above a helium bubble is turned up due to the bursting of the helium bubbles. The concavity and convexity created the bursting of the helium bubble are enhanced by the repetition of the bursting of helium bubbles at the region around cavity. Consequently, the concavity and convexity forms the tungsten fuzzy nanostructure.

The tungsten fuzzy nanostructure is surely important problem for use as divertor materials. The present multi-scale and multi-physical simulation approach continues to the solvation of future problems of fusion reactor materials. In addition, the tungsten fuzzy nanostructure is interesting as a scientific problem and plasma applications also. By this point, the research field of fusion reactor materials had gotten many collaborators from the research field for material science with powerful methods. A continuation of the collaboration will advance nuclear fusion projects in future.

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