

Molecular Dynamics Study of Ballistic Rearrangement of Surface Atoms during High Energy Ion Bombardment on Pd (001) Surface

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ABSTRACT

Atomic behavior during ion bombardment was investigated by using three dimensional classical molecular dynamics (MD) simulation. It was observed that significant amount of surface atoms were rearranged when Ar ions bombarded the Pd (001) surface in addition to the erosion of surface atoms. Quantitative analysis showed that the rearranged atoms are three times as many as sputtered atoms regardless to the energy and angle of incidence ions. Contrary to the conventional concepts which describe the surface structure evolution based on the erosion theory, the rearranged atoms were turned out to play a significant role in forming the surface morphology as shown in the simulated surface morphology by the bombardment of many Ar ions.

Keywords: molecular dynamics, ion beam sputtering, surface structure

1 INTRODUCTION

High energy ion bombardment on solid surface has attracted much attention owing to its capability to fabricate ordered nanoscale structures such as self aligned quantum dots [1]. Moreover, it is worth while considering a peculiar technology beyond the conventional approach such as 'Top-down' and 'Bottom-up'. The simplest application of ion bombardment is to collect the sputtered atoms on the substrate to form a thin film. Most researchers have utilized sputtering as deposition tool and they focused on the reaction phenomena between recoiled ions from the target and substrate atoms to deposit. However, since a suggestion by Facsko *et al.* was introduced, it has taken an enormous attention to researchers whose aim was to manufacture the nano patterns on the surface [1]. Such a peculiar process resulted in enhancing the possibility for designing nano sized patterning by cheap and simple method.

Using this technique, it can be applied to various aspects such as the ordered adsorption of large molecules [2], optoelectronic devices [1], molding templates [3], manipulating magnetism [4,5], tuning the chemical reactivity of catalytically active surface [6] and for manipulating film texture [7] *etc.* Also there are many results for obtaining various nano patterns with respect to the incident energy, angle of ion source, temperature, and substrate materials [8-11].

Theoretical studies on the ion bombardment have been developed based on the Sigmund's theory [12] and Bradley-Harper (BH) instability model [13]. It is assumed in these theoretical works that the surface roughening or structure evolution by ion bombardment was proportional to the sputter yield. However, some results based on the atomistic simulation were reported that ion bombardments result in not only erosion of target atoms but also rearrangement on the surface [14, 15]. As an example, Fig. 1 shows the result of the atomic configuration when Ar ion with 10 keV energy bombarded on Au (001) surface by using MD simulation. This dynamic simulation evidently shows that some atoms were sputtered from the surface and some of the surface atoms form a rim around the crater by ballistic rearrangement.

In this work, we focused on the rearrangement of the surface atoms to reveal the mechanism of surface structure evolution during the high energy Ar bombardment on Pd (001) surface. To obtain quantitative data, statistical analysis was performed for 1,000 events of Ar bombardment on randomly chosen surface position. We also simulate the surface structure evolution by sequential Ar bombardment. Autocorrelation function of the bombarded surface was employed to characterize the representative surface pattern.

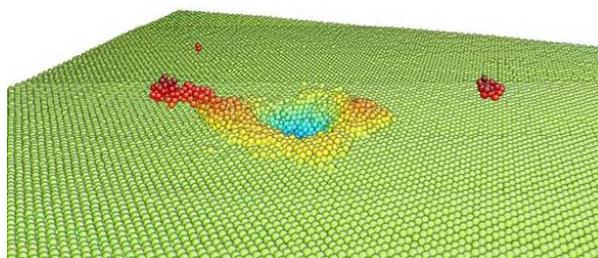


Figure 1: Snapshot of atomic configuration during Ar bombardment on Au (001) with 10 keV incident energy.

2 CALCULATION PROCEDURE

The accuracy of MD is largely dependent on the reliability of interatomic potential in use. In this work, two kinds of interatomic potentials were combined and utilized for simulating ion bombardment. To describe the thermal and mechanical behaviors of the materials, we used embedded atom method (EAM) potential which is well-known and reliable for the metallic system such as Pd [16].

EAM potential is expressed as follows:

$$E_{tot} = \frac{1}{2} \sum_{i,j(i \neq j)} \phi(r_{ij}) + \sum_i F_i \left(\sum_{j \neq i} \rho_j(r_{ij}) \right) \quad (1)$$

Here, $\phi(r_{ij})$ is a pairwise interaction between atoms at a distance between i and j atoms, $\rho_j(r_{ij})$ is electron density contributed by atom j . With this approximation for the electron density, the effect of electrons on individual ions can be simply but efficiently described. Using embedding function $F(\rho)$, energy can be obtained from the electron density. Coupling with the electron density functions, many-body properties such as crystal structure, stacking fault energy, and phase stability can be described.

For describing highly repulsion behavior at short distance, we used Ziegler, Biersack and Littmark (ZBL) potential [17] which is composed of Coulombic potential and screening function. ZBL potential is the most commonly used in ion bombardment simulations and it is related to the atomic number Z_1 and Z_2 . This function is expressed as the product of the Coulombic potential and a screening function as follows:

$$V(R) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R} \sum_{k=1}^N c_k \exp(-b_k R/a) \quad (2)$$

where e is the electron charge, ϵ_0 is the permittivity of vacuum, R is the interatomic distance between two atoms. In the screening function, c_k and b_k are the coefficients defined differently for potentials and each value listed in table 1. a is the screening length which is given by

$$a = \frac{0.8856 \times a_0}{Z_1^{0.23} + Z_2^{0.23}}, \quad (3)$$

where $a_0 = 0.529\text{\AA}$ is the Bohr length.

When Ar atom collides with Pd atoms with high energy, atomic states far from their equilibrium position should be simulated. EAM potential is generated based on the data of near equilibrium state. Therefore, to describe the high energy ion collisions more accurately, pairwise potential, $\phi(r_{ij})$, should be modified by joining smoothly to the ZBL potential at small separations. To avoid splining errors and derivative discontinuity problem, switching function should be utilized for interpolating between EAM-pair and ZBL potential. Switching function is generally formed as follows:

$$V(r) = V_{ZBL}(r)S(r) + V_{EAM}(r)(1-S(r)) \quad (4)$$

which is applied in a region $r_1 < r < r_2$, and has the following properties: $S(r_1)=1$, $S(r_2)=0$ and $S'(r_1)=S'(r_2)=0$. We used cosine function as follows:

$$S(r) = \frac{1}{2} \cos\left(\frac{r-r_1}{r_2-r_1} \pi\right) + \frac{1}{2} \quad (5)$$

The potentials used in this study were rigorously benchmarked by using the calculated or experimental observed physical properties of Pd.

In this study, we investigated atomic behavior around the surface when highly accelerated Ar ion impacts on the Pd (001) surface with various energies and incident angles.

To elucidate the atomic reaction on the surface, one thousand individual trials were performed for statistics and quantitative parameters such as sputtering yield (Y_{spt}), rearrangement yield (Y_{rear}) were extracted. Moreover, spatial distribution of these behaviors also obtained after normalizing process. To show the effect of the incident energy of Ar ion, we selected 0.5, 1.0 and 2.0 keV energy and to show the effect of the incident angle, we selected 0 (normal), 30, 45, 60 and 75 degrees of incident angle with projecting toward [011] direction. Considering Ar incident energy, the substrates were prepared 3-types which scale is large enough for Ar and substrate atoms to react without simulation errors. The size of the substrate for 0.5, 1.0, and 2.0 keV was $20 \times 20 \times 20$ (a_0^3), $24 \times 24 \times 20$ (a_0^3) and $30 \times 30 \times 30$ (a_0^3), where a_0 is equilibrium lattice constant for each metal and total number of the substrate atoms was 32,000, 46,080 and 108,000, respectively. All calculations were performed by using LAMMPS code [18].

i	1	2	3	4
c_i	0.1818	0.5099	0.2802	0.02817
b_i	3.2	0.9423	0.4029	0.2016

Table 1: Parameters used in screening function.

3 RESULTS AND DISCUSSION

We computed Y_{spt} from the total amount of sputtered atoms for various simulation conditions. Figure 2(a) shows the change of Y_{spt} as a function of incident energy and angle. The unit of Y_{spt} is the number of atoms per incident ion. Y_{spt} varies with the incident angles and the highest yield was obtained at the incident angle of 60 degrees. Such a tendency becomes more obvious as the incident energy increased. However, Y_{spt} were decreased rapidly after 60 degrees and near zero sputter yield was obtained at 75 degrees. We also computed Y_{rear} by counting the total atoms which remained above the original surface after the bombardment. Figure 2(b) shows the change of Y_{rear} at same conditions of Y_{spt} (Fig. 2(a)). The tendency for the incident angle was similar to that of Y_{spt} . However, it must be noted that the value of Y_{rear} was much larger than that of Y_{spt} .

The ratio between Y_{spt} and Y_{rear} was in the range of 2.8 ± 0.4 regardless of the incidence energy and incidence angle. This means that when Ar ion bombards on the Pd (001) surface, Y_{rear} was always shown to be about 3 times larger than Y_{spt} . It was reported that when Xe atom bombards on the Pt (111) surface, the ratio was almost constant in the range from 3 to 5 [19,20]. Similar results have been reported in various systems [21-23]. Our simulation results are in good agreement with the previous report on the ratio between erosion and rearrangement. The present results show that the surface morphology in nano meter scale should be investigated based on the new concept or model that includes the effect of the rearranged atoms.

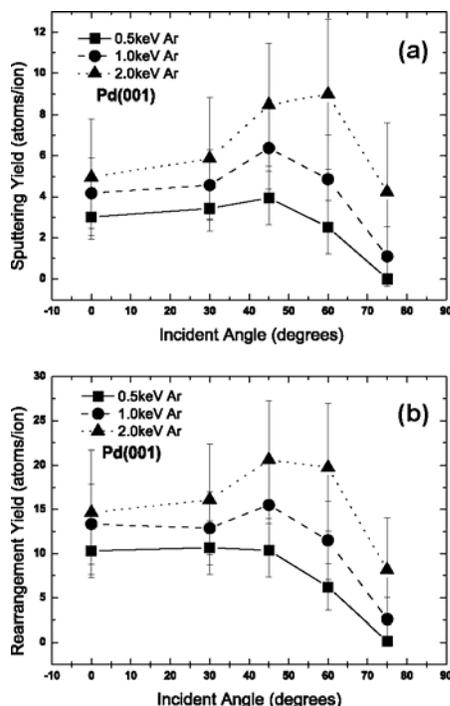


Figure 2: (a) Sputtering and (b) rearrangement yields with respect to the incident energy and angle of Ar on Pd (001). Error bars denote the standard deviation of each case.

To confirm the rearrangement effect on the formation of surface patterns, many Ar atoms were bombarded on the Pd (001). The position of bombarding Ar was randomly selected in the x and y direction. The Ar atoms of 0.5 keV of incident energy bombarded the surface in surface normal. Fig. 3 (a) shows the surface morphology after 4,200 bombardments of Ar atoms. The colors of each atom denote the relative height of the atoms. Orange color denotes the initial surface height. Blue one is an atom which locates lower than initial surface, while the red one is an atom which locates higher than initial surface due to the rearrangement of surface atoms. From the data shown in Fig. 2 (a), 4,200 Ar bombarding would sputter 12,600 (3.9 ML) Pd atoms. Even though such a large number of Pd atoms were eroded, some areas on the surface are still remained higher than the initial surface. It is evident in Fig. 3 (a) that the rearranged atoms play an important role in evolving the surface patterns.

In order to investigate the qualitative analysis of the surface pattern, two dimensional autocorrelation function of Fig. 3 (a) surface was calculated. Fig. 3 (b) is the autocorrelation function, which reveals that the correlation image is a little distorted diamond shape along $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. This result is in consistent with an experimental result [24] that shows the diamond-shape autocorrelation function. It must be noted that this calculation did not consider the long range surface diffusion but the ion induced ballistic rearrangement. It can be thus said that the long range diffusion would be negligible in the surface morphology evolution.

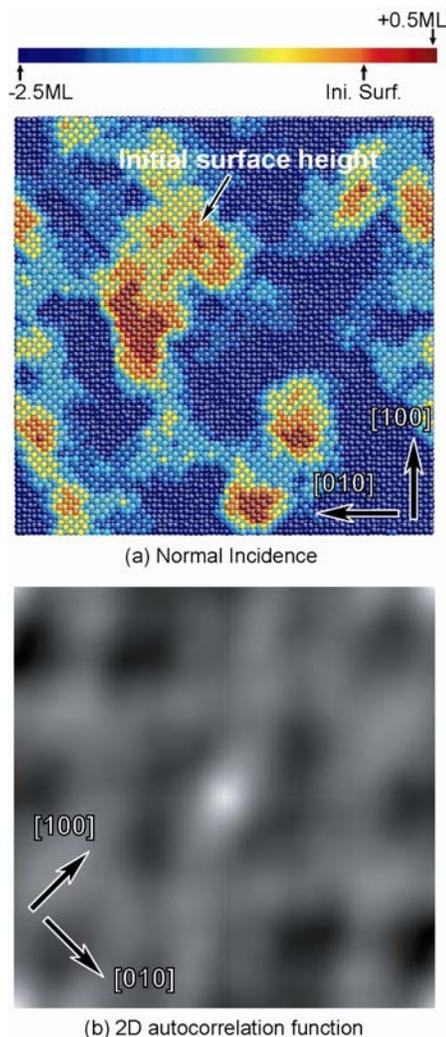


Figure 3: (a) Atomic configuration after 4,200 (1.73×10^{15} ions/cm²) Ar bombardments on Pd(001) surface (15.56×15.56 nm²). Color depth denotes the height. (b) 2D autocorrelation function image of (a).

The 4 fold symmetry in the surface morphology is closely related to the distribution of the rearranged atoms. The lateral distribution of the rearranged atoms was computed by analyzing statistically the molecular dynamic simulation results. The lateral positions of rearrangement atom were normalized by the impact point. Fig. 4 shows the lateral distribution of the rearranged atoms when Ar atoms of 0.5 KeV bombarded the Pd (001) surface in normal direction. The intensity of the color denotes the degree of probability of rearranged atoms. The shape of the distribution has the 4 fold symmetric features where the edges are parallel to the $\langle 110 \rangle$ direction. It can be said that the 4 fold anisotropic surface pattern of Fig. 3 results from the accumulation of the rearranged atoms of the anisotropic lateral distribution as shown in Fig. 4.

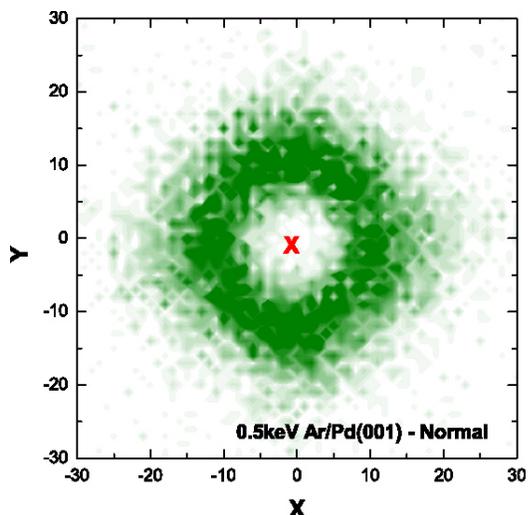


Figure 4: Lateral distribution of rearrangement atoms on Pd(001) with 0.5 keV Ar ion bombardments for normal incidence. x axis coincides with $\langle 100 \rangle$ direction and y axis with $\langle 010 \rangle$ direction of (001) surface. 'X' means the normalized impact point.

4 CONCLUSION

The most significant result of the present work is to show that significant rearrangement of the surface atom occurs during high energy ion bombardment. Because the number of rearranged atoms is much larger than that of sputtered atoms, the surface structure evolution during ion bombardment can be dominated by the distribution of the rearranged atoms. This result suggests that the kinetic theories of the surface structure evolution include the concept of the rearranged atoms in addition to the negative deposition concept.

The present simulation of Ar ion bombardment on Pd (001) surface also demonstrates the formation of 4 fold symmetric autocorrelation of the surface. By quantitative analysis of lateral distribution of rearranged atoms, we could conclude that ballistic rearrangement of the surface atom plays a significant role in the surface structure evolution. These results are in good agreement with the previous experimental observation.

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REFERENCES

[1] S. Facsko, T. Dekorsy, C. Koerdts, C. Trappe, H. Kurz, A. Vogt, and H. L. Hartnagel, *Science* 285, 1551, 1999.
 [2] P. Chaudhari, J. Lacey, J. Doyle, E. Galligan, and S. C. A. Lien, *Nature* 411, 56, 2001.

[3] O. Azzaroni, P. L. Schilardi, R. C. Salvarezza, R. Gago, and L. Vazquez, *Appl. Phys. Lett.* 82, 457, 2003.
 [4] Y. J. Chen, J. P. Wang, E. W. Soo, L. Wu, and T. C. Chong, *J. Appl. Phys.* 91, 7323, 2002.
 [5] R. Moroni, D. Sekiba, B. Mongeot, G. Gonella, C. Boragno, L. Mattera, and U. Valbusa, *Phys. Rev. Lett.* 91, 167207, 2003.
 [6] L. Vattuone, U. Burghaus, L. Savio, M. Rocca, G. Costantini, F. Mongeot, C. Boragno, S. Rusponi, and U. Valbusa, *J. Chem. Phys.* 115, 3346, 2001.
 [7] K. C. Ruthe, and S. A. Barnett, *Surf. Sci.* 538, L460, 2003.
 [8] W. L. Chan and E. Chason, *J. Appl. Phys.* 101, 121301, 2007.
 [9] M. J. Aziz, *Ion Beam Science: Solved and Unsolved Problems* 52, 187, 2006.
 [10] S. Vogel and S. J. Linz, *Europhys. Lett.* 76(5), 884, 2006.
 [11] U. Valbusa, C. Boragno, and B. Mongeot, *Mater. Sci. and Eng. C* 23, 201, 2003.
 [12] P. Sigmund, *J. Mater. Sci.* 8, 1545, 1973.
 [13] R. M. Bradley, and J. M. E. Harper, *J. Vac. Sci. Technol. A* 6(4), 2390, 1988.
 [14] A. Friedrich, H. M. Urbassek, *Surf. Sci.* 547, 315, 2003.
 [15] E. M. Bringa, K. Nordlund, and J. Keinonen, *Phys. Rev. B* 64, 235426, 2001.
 [16] S. M. Foiles, M. I. Baskes and M. S. Daw, *Phys. Rev. B* 33, 7983, 1986.
 [17] J. F. Ziegler, J. P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York 1985).
 [18] S. J. Plimpton, *J. Comp. Phys.* 117, 1, 1995.
 [19] H. Gades, H. Urbassek, *Phys. Rev. B* 50, 11167, 1994.
 [20] P. Mishra, and D. Ghose, *Phys. Rev. B* 74, 155427, 2006.
 [21] H. Hansen, A. Redinger, S. Messlinger, G. Stoian, Y. Rosandi, H. M. Urbassek, U. Linke, and T. Michely, *Phys. Rev. B* 73, 235414, 2006.
 [22] G. Costantini, B. Mongeot, C. Boragno, and U. Valbusa, *Phys. Rev. Lett.* 86, 838, 2001.
 [23] C. Busse, H. Hansen, U. Linke, and T. Michely, *Phys. Rev. Lett.* 85, 326, 2000.
 [24] T. C. Kim, C. M. Ghim, H. J. Kim, D. Y. Noh, N. D. Kim, J. W. Chung, J. S. Yang, Y. J. Chang, T. W. Noh, B. Kahng, and J. S. Kim, *Phys. Rev. Lett.* 92, 235414, 2006.