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Cluster Size Effect on Surface Modification Process Using Cluster Ion Beam

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Computer simulations and experiments were performed in order to understand the effect of cluster size on surface modification process by cluster ion irradiation. Molecular dynamics simulations of clusters impacting on solid targets derived the model function that explains the relationship among cluster size, incident energy and number of displacements. On the other hand, the time-of-flight study of gas cluster ion beam revealed that cluster size distribution could be controlled by changing ionization conditions. The irradiation effect under various irradiation conditions were examined using RBS and AFM. The results from computer simulations and experiments showed good agreements in the results that surface damage and roughening were reduced at the impact of larger size cluster. These results suggest that high-performance surface process will be achieved by gas cluster ion beam technique with selecting cluster size distribution and incident energy.

Key words: cluster ion beam, size selection, damage formation, molecular dynamics simulation

1. INTRODUCTION

Cluster is an aggregated material of atoms or molecules. The impact process of cluster and solid target is very different from that of monomer ion because of innumerable collisions between cluster and surface atoms, which is termed as 'non-linear process' [1]. The non-linear processes of cluster impacts have been expected to realize high-performance surface processes. For last decade, gas cluster ion beam (GCIB) technique [2] has been developed. GCIB technique makes it possible to generate intense cluster ion beam which consists of large size (several thousands) clusters, and can be introduced to industrial applications, such like surface smoothing [3] and thin film formations [4].

The non-linear effect of cluster impact depends on various parameters of cluster ion irradiation, such like the atomic species, incident energy and cluster size. In order to introduce the GCIB process to industrial applications, it is important to clarify the relationship between the non-linear effect and the irradiation condition of cluster ion. In this work, both computer simulations and experiments were performed in order to examine the cluster size effect on the damage formation. The efficiency of the development of size control technique for cluster ion beam was discussed.

2. COMPUTER SIMULATION OF CLUSTER IMPACT

Molecular dynamics (MD) simulation is one of the powerful methods to understand the collisional process of cluster on solid surface. In this work, the similar simulation conditions to experiments were carried out. Ar clusters with the size ranging from 10 to 20000 were irradiated on Si (100) target at total incident energy of 10, 20 and 50keV. The inter-atomic potentials were described with Stillinger and Weber model [4] for Si-Si, and ZBL (Ziegler, Littmark, and Biersack) model [5] was applied for the interactions between Si and Ar atoms, and Ar atoms themselves. Large Si (100) target which consists of about 2,000,000 atoms, with the dimensions of 400Å×400Å×200Å was prepared as a target material. This is because that irradiated Si target should be large enough to receive the energy induced by cluster impact; for example, when 50keV of total energy are deposited on the target, each target atom gains 0.025eV. As for boundary conditions, the surface where a cluster impacts was under free-boundary, while the bottom end was fixed keeping bulk structure. For the other two lateral directions, periodic boundary conditions were applied. The MD simulations were performed for 16ps, which is long enough to observe the impact process of cluster and solid target, such like penetration and re-evaporation of cluster atom, formation and relaxation of displaced target atoms.

Figure 1 shows the MD snapshots of Ar clusters with various sizes impacting on Si (100) surface. The total incident energy was set to 20keV. Each snapshot is drawn from sliced substrate with 40Å thickness including the impact point. Black and white circles indicate Ar and Si atom, respectively. Especially, circles filled with gray indicate displaced Si atoms. The displacements were defined as the atoms that were below 2.5Å from the surface level and that their potential energies were above 0.2eV from bulk status [6]. Figure 1 indicates that the amount and structure of damage strongly depend on cluster size. When cluster size is in a range from several hundreds to several thousands, a large number of Si atoms are displaced spherically and a crater-like damage remains on the surface after the re-evaporation of incident Ar atoms. This crater-like damage is confirmed by in-situ STM observation of Si surface bombarded with Ar cluster ions [7]. When cluster size is as small as 20, the diameter of the crater decreased to 20Å, but dense

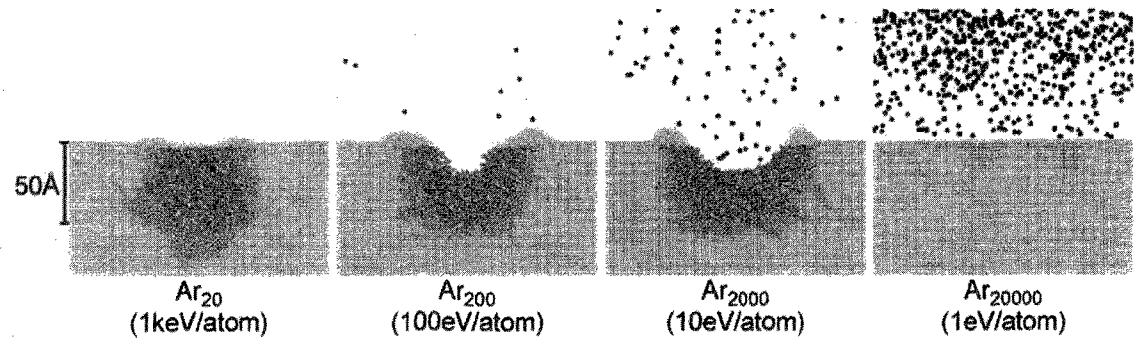

Fig. 1: MD snapshots of Ar cluster with various sizes (total energy is 20keV, 16ps after impact).

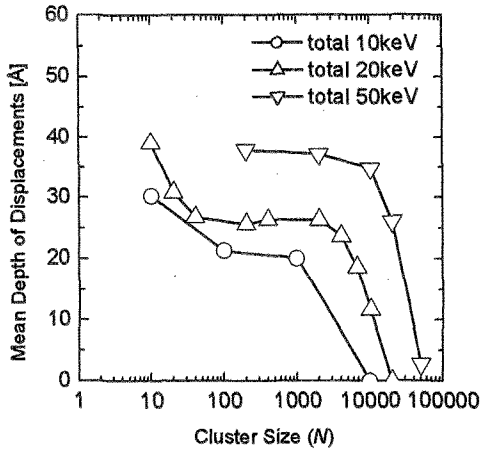

Fig. 2: Cluster size dependence of mean depth of displacements by Ar clusters total acceleration energies of 10, 20 and 50keV.

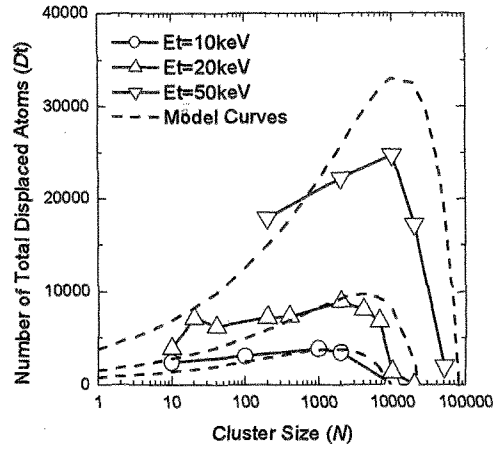

Fig. 3: Cluster size dependence of total number of displacements by Ar clusters with total acceleration energies of 10, 20 and 50keV. The dashed lines are model functions given by Eq. (1).

damaged region remains in the surface and these displacements shows deeper depth profile than those by Ar_{200} and Ar_{2000}. On the other hand, when the cluster size is as large as 20000, and incident energy is as low as 1eV/atom, the cluster does not penetrate the surface but breaks up on the surface. During this collisional process, some surface atoms are displaced, but theirs displaced length is small. Therefore, these displacements recover and no damage remains on the surface within several pico-seconds after the impact.

Figure 2 shows the mean depths of displacements induced by Ar clusters with various sizes and energies. The mean depth of displacements decreases as a cluster size increases. However, there is a cluster size regime where mean depth is kept constant. This result agrees with the fact that the shapes of craters by clusters in this size regime are similar with each other as shown in Fig. 1. When a cluster size is set in this regime and impacts with the solid surface, the cluster can penetrate the surface keeping itself in cluster state. A large number of interactions between cluster and surface atoms are caused. Through these collisions, almost all of kinetic energy of cluster is transferred to substrate to cause crater structure. Because of this collisional process, similar crater shapes remains with clusters with these cluster sizes [8].

Figure 3 shows the cluster size dependence of number of displacements at the total incident energy of 10, 20 and 50keV. From the simulation data, the model curve is proposed to describe the number of displacements (D_t) as a function of cluster size (N) and total incident energy (E_t) as follows [9],

$$D_t(N, E_t) = A_1 (N^{\alpha} E_t - T_1 N^{\alpha+\tau+1}), \quad (1)$$

where

$$T_1 = 10.38[\text{eV}], \tau = -0.25$$
$$A_1 = 0.076[\text{atoms/eV}], \alpha = 0.26 \quad (2)$$

The parameters T_1 and A_1 indicate the threshold energy to cause damage and yield of damage formation for Ar monomer, respectively. This formula represents the characteristics of damage formation depending on cluster size. At the E_t of 20keV, for example, D_t reaches maximum at the cluster size of several thousands and gives 0 at the size of several tens of thousands. Eq. (1) gives the cluster sizes where a cluster causes no displacement (N_0) or maximum number of displacements (N_m). These characteristic cluster sizes are given by,

$$N_0 = \left(E_t / T_1\right)^{\frac{1}{\tau+1}} = \left(E_t / T_1\right)^{1.33} \quad (3)$$

and

$$N_m = \left(\frac{\alpha}{\alpha+\tau+1}\frac{E_t}{T_1}\right)^{\frac{1}{\tau+1}} = 0.146 N_0. \quad (4)$$

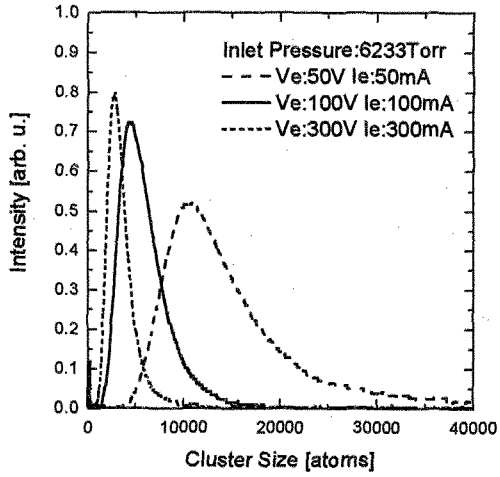

Fig. 4: Cluster size distribution measured by TOF at various ionization voltage (Ve) and current (Ie).

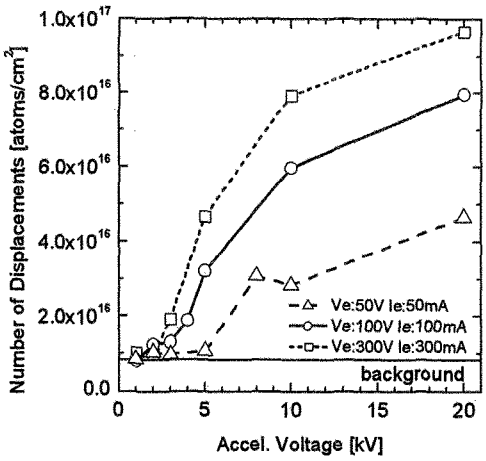

Fig. 5: Incident energy dependence of number of displacements at various cluster size distributions. *Each line style corresponds to similar style shown in* Fig. 4.

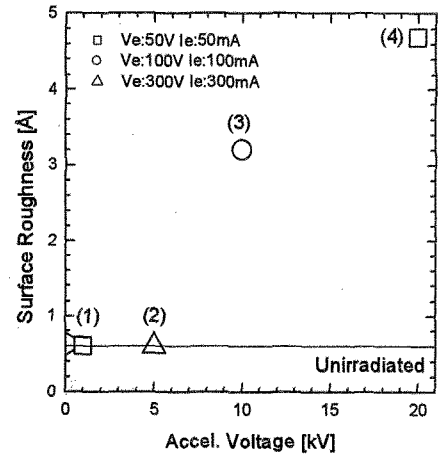

Fig. 6: Surface roughness of Si substrates before and after irradiations of Ar clusters at various sizes and energies.

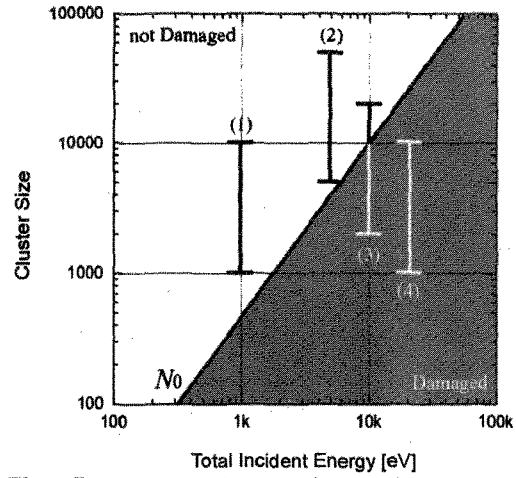

Fig. 7: Correspondence of experimental and simulation results from the viewpoint of size distribution and damage formation.

Figures 2 and 3 suggest that the amount and depth of displacements can be controlled by changing cluster size and energy. This is an advantage for high-performance surface processes in nano-scale. As for surface smoothing and etching process, large motion of atoms at near surface region is preferred without deep damage [3]. As shown in Figs. 2 and 3, it can be found that the cluster with the size around N_m gives maximum density of displacements, which is expected to result in the most effective motion of surface atoms. On the other hand, when cluster ion beam is applied to assist the thin film formation [4], cluster size above N_0 will be selected in order to reduce damage and cause high-density atomic irradiation.

3. EXPERIMENTS OF CLUSTER SIZE CONTROL AND DAMAGE FORMATION

Cluster size dependence of surface modification process was studied experimentally [10]. Figure 4 shows the time-of-flight (TOF) mass spectra of cluster beams at various ionization voltages and current. The previous work reported that, the higher inlet gas pressure contributes to the generation of large size clusters [11]. In this study, very large cluster with 15000 in mean cluster size was obtained. Figure 4 also indicates that, as the ionization voltage and current increase, the cluster size distribution decreases. At 300V and 300mA of ionization voltage and current, the mean cluster size is reduced to 2500. It is considered that, the high-energy electron bombardment with large ionization current induces multiple ionization or thermal excitation of cluster, which results in the corruption of large clusters.

Cluster ion beams with above-mentioned size distribution were irradiated on Si substrates and number of displacements was measured using Rutherford backscattering spectrometry (RBS). Figure 5 shows the incident energy dependence of the number of displacements at various cluster size distributions. For each irradiation condition, the ion dose was 1.0×10^{15} ions/cm^2. In Fig. 5, the style of each line corresponds to the one of size distribution shown in Fig. 4. As shown in Fig. 5, damage formation by cluster ion depends on the

cluster size distribution. When cluster size increases, the total number of displacements decreases and the threshold energy to cause damage increases. Additionally, irradiated surfaces were measured by atomic force microscope (AFM). Figure 6 shows the surface roughness in 1μm×1μm area of Si substrates before and after cluster irradiations. The irradiation conditions shown in Fig. 6 are,

(1) Ve: 300V, Ie: 300mA (small size), Va: 1keV
(2) Ve: 50V, Ie: 50mA (large size), Va: 5keV
(3) Ve: 100V, Ie: 100mA (medium size), Va: 10keV
(4) Ve: 300V, Ie: 300mA (small size), Va: 20keV,

where Ve, Ie and Va are ionization voltage, ionization current and acceleration voltage, respectively. As shown in Fig. 6, it is found that surfaces do not become rough with irradiations with conditions (1) and (2), while conditions (3) and (4) make surfaces rough. Figures 5 and 6 agree with each other in cluster size and incident energy dependence of damage formation.

The correspondence of experimental results with the model predicted by MD simulations is shown in Fig. 7. In Fig. 7, the thick line indicates the relation between N_0 and total energy given by Eq. (3). The index numbers (1)~(4) correspond to the experimental conditions shown in Fig. 6 and the range of cluster size distribution at each condition is indicated with the length of vertical bar. As shown in Figs. 5, 6 and 7, the experimental results show good correlations with the MD prediction. For example, in the case of condition (2), all of cluster sizes are larger than N_0, which means that damage cannot be induced by those cluster impacts. On the other hand, in the cases of conditions (3) and (4), some and whole part of the size distributions span over N_0, respectively. The magnitude of damage and surface roughening shown by experiments represent well the ratio of cluster sizes under N_0.

4. SUMMARY

Cluster size effect on surface modification process was studied by both simulation and experimental methods. Molecular dynamics simulations of Ar cluster impacts on Si substrates leaded the model function to describe the number of displacements depending on cluster size and incident energy. The model function revealed that, when total incident energy is constant, the number of displacements increases with increasing cluster size, but there is specific number (N_m) to cause maximum number of displacements. If the cluster size is larger than N_m, the damage is reduced as the cluster size increases and reaches the size where no displacement is generated (N_0). As for the depth of damage, it is found that there is a cluster size regime where mean depth is kept constant. This cluster size regime ranges from several tens atoms to N_m. These results suggest that a cluster with its size of around N_m is expected to cause most effective surface motion for sputtering and surface smoothing.

The time-of-flight measurements of gas cluster ion beams showed that the cluster size distribution could be changed with the change of ionization condition. As the ionization current and voltage increase, the size distribution in cluster ion beam was shifted smaller because multiple ionization and thermal excitation cause corruption of large clusters. Ar cluster ion beams with various size distributions were irradiated on Si target and induced damages were measured with RBS and AFM. It was found that the amount of damage is different depending on cluster size distribution. As the mean cluster size increases, both displacements formation and surface roughening were reduced. Through these experiments, no damage irradiation can be achieved with several irradiation conditions. These no-damage irradiation conditions agreed with the predictions by MD simulations. These results conclude that cluster size technique is important and useful to realize various irradiation processes using cluster ion beam.

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