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ADATOM, VACANCY AND SPUTTERING YIELDS OF ENERGETIC Pt ATOMS IMPACTING ON Pt(100) BY MOLECULAR DYNAMICS SIMULATION*

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We have studied the influence of incident atoms with low energy on the Pt(100) surface by molecular dynamics simulation. The interaction potential obtained by the embedded atom method (EAM) was used in the simulation. The incident energy changes from 0.1eV to 200eV, and the target temperature ranges from 100 to 500 K. The target scales are 6×6×4 and 8×8×4 fcc cells for lower and higher incident energies, respectively. The adatom, sputtering, vacancy and backscattering yields are calculated. It was found that there is a sputtering threshold for the incident energy. When the incident energy is higher than the sputtering threshold, the sputtering yield increases with the increase of incident energy, and the sputtering shows a symmetrical pattern. We found that the adatom and vacancy yields increase as the incident energy increases. The vacancy yields are much higher than those obtained by Monte Carlo simulation. The dependence of the adatom and sputtering yields on the incident energy and the relative atomistic mechanisms are discussed.

Keywords: molecular dynamics simulation, sputtering yield, adatom yield, film growth
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I. INTRODUCTION

Plasma-assisted deposition is one of the important film synthesis methods. In the past years, various plasma-assisted film-growth methods have been developed, such as reactive magnetron sputtering (RMS), plasma-enhanced physical vapour deposition (PEPVD), and plasma-enhanced chemical vapour deposition (PECVD), etc. In the plasma-assisted deposition a negative bias voltage is often applied, so that energetic particles play a very important role. Due to the effects of energetic particles (ions and energetic atoms) in the plasma on the film growth, the growth mode and preferred orientation of the films can be changed. Moreover, the density of film, the smoothness of the film surface, and the adhesion of the film to the substrate are considerably improved. Therefore, it is very important not only for fundamental theory, but also for technology and applications to understand the film growth at an atomic level.

Webb and Harrison[1] have predicted theoretically the production of adatoms on a surface due to energetic ion bombardment in the molecular dynamics (MD) simulation of 5 keV Ar ions impacting on a Cu(100) surface. In the simulation of low-energy Pt atoms deposited on Pt(111), Villarba and Jönsson observed the 'push-out' events, where the incident atoms displace the peripheral island atoms. Push-out events lead to the incorporation of the incident atoms in the growing layer and, thereby, can contribute to layer-by-layer growth if islands are small enough. To some extent, the 20eV incident energy also produces detrimental effects, such as the displacement of surface atoms, vacancy formation, and displacement of island atoms to a position on top of the growing layer, thus promoting multilayer growth. Michely and Teichert determined the adatom yield and the sputtering yield, using scanning tunnelling microscopy (STM) methods, for noble-gas ions incident on Pt(111).[3] They also found that the dependence of adatom and sputtering yields on ion energy and ion mass is not in agreement with previous theoretical predictions. Meanwhile, Breemann and Boerma[4] have observed adatom generation by ion bombardment on Cu(100) with low-energy ion scattering. The morphology of the (100) face of copper after sputtering with 600 eV Ar ions has been investigated by using STM by Girard *et al.*[5] They found that at low flux, vacancy as well as adatom islands coexist, and the removal mode is three-dimensional, whereas at high flux, adatom islands disappear, and the removal mode becomes two-

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dimensional, that is, layer-by-layer growth. Brice *et al.*[6] have utilized Monte Carlo calculations to study the displacements of surface and bulk atoms by energetic incident ions. They concluded that molecular-dynamics simulations are needed for low energies in order to examine more accurately the energy regime where the threshold for surface-atom displacements occurs. It has been testified that molecular-dynamics simulation is the only effective simulation that can offer the detailed motion of low-energy incident atoms during the growth of a thin film. Although TRIM (a computer program) can give some information about sputtering and vacancy yields, it becomes increasingly questionable at energies below 100 eV.

In this paper, we study the process of low-energy incident atoms impacting on a Pt(100) surface by MD simulation with the atomic potential obtained by the embedded atom method (EAM).[7] We describe the variation tendency of the adatom, sputtering and vacancy yields with the increase of incident energy. We also study the dependence of adatom, sputtering and vacancy yields on the incident energy and the substrate temperature.

II. SIMULATION METHODS

The EAM potential was employed to describe the interaction of Pt atoms in the simulation. The EAM has been found to be an effective way to investigate the properties of surface and bulk for fcc (face-centred-cubic) metals.[8] The simulation was carried out with low-energy atoms impacting on a Pt(100) surface. The substrates were modelled with 6×6×4 fcc cells and 8×8×4 fcc cells for the incident energy lower and higher than 100eV, respectively. Periodic boundary conditions were used in the plane that is parallel to the surface. To avoid the substrate from moving by the impacts of the energetic incident atoms, the positions of the atoms in the lowest three layers were fixed. Before the introduction of a new atom, the velocity of the movable atoms in the substrate were set in Boltzmann distribution according to the substrate temperature. The position of the incident atom was randomly set in the scale of an fcc cell. The incident atom ran to the substrate surface vertically from where it had negligible interaction with the surface. The substrate was controlled to act as a constant-temperature system. The constant-temperature condition was applied to the atoms in the substrate by using the method similar to that suggested by Berenden.[9] To keep the mobility of atoms on the surface, a surface layer was defined, and the atoms were not restrained by the constant-temperature condition. The model has been described in detail elsewhere.[10−11] The energy of the incident atoms ranged from 0.1eV to 200eV. The substrates were kept at temperatures 100K, 300K and 500K so that we could investigate the influence of substrate temperature on the incident processes. It has been found that it takes about 3ps for the substrate to return to the original temperature.[11] Hence the total time of a single incident atom from the beginning of the drop until the atom stops on the surface is 6ps.

III. RESULTS AND DISCUSSION

A. Evolution of kinetic energy of incident atoms

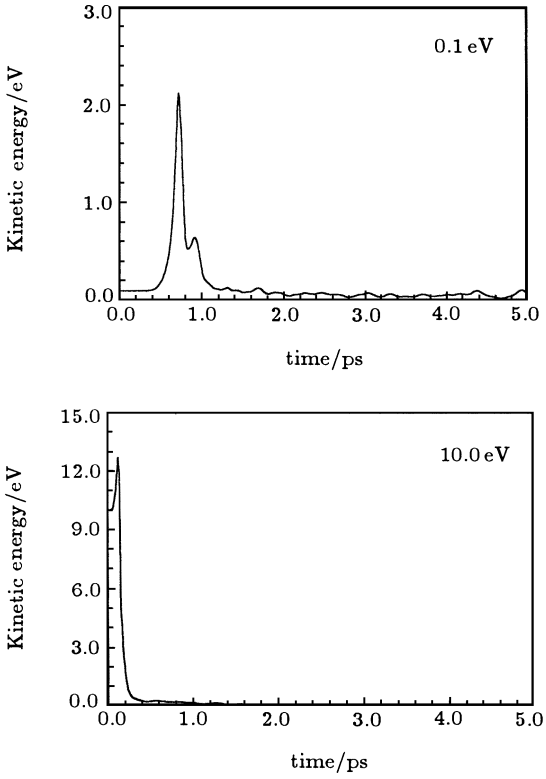


Fig.1. Evolution of kinetic energy of incident atoms.

Figure 1 shows the evolution of the kinetic energy of incident atoms with time. The results are those averaged over 50 deposition events and the initial substrate temperature is 300 K. In the figure, we can see that the kinetic energy of the incident atom increases first, and the increment is about 2–3 eV, which originates from the latent heat of binding energy. The kinetic energy of incident atoms increases from the beginning to its maximum value in about 0.2–0.3 ps and then drops very sharply. After that, the kinetic

energy dissipates in the form of damping oscillation in 1–2 ps. It is very interesting that the time spent in the process of kinetic energy dissipation of incident atoms is not obviously dependent on the incident energy of deposited atoms. The result implies that the incident atom loses its kinetic energy in a very short time (about 0.2–0.4 ps) after impinging on the surface. The excess energy dissipation of deposited atoms in the form of damping oscillation resulted from the diffusion of thermal energy in the local environment.

B. Sputtering yields

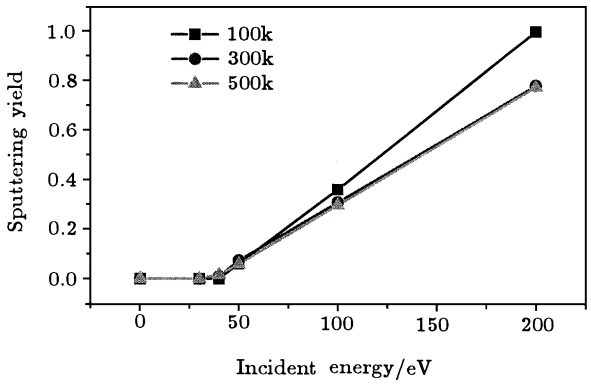


Fig.2. Sputtering yields of incident Pt atoms with 0.1eV to 200eV on Pt(100) surfaces. The substrate temperatures are 100K, 300K and 500K.

Figure 2 presents the sputtering yield (Y_s) data obtained for energetic Pt atoms impacting on Pt(100) surfaces at 100K, 300K and 500K with the incident energy ranging from 0.1eV to 200eV. The sputtering yields exhibit the following characteristics:

(i) There is a sputtering threshold of about 40eV for the incident energy. The incident atoms with an energy lower than the sputtering threshold cannot transfer enough energy to the substrate atoms to overcome the binding energy barrier and thus no sputtering occurs. In other words, the incident atoms with an energy below the sputtering threshold are deposition atoms.

(ii) The sputtering yields increase with the increase of incident energy when the energy of incident atoms is higher than the sputtering threshold. The yields depend on the energy of incident atoms as expected qualitatively from the linear cascade theory.[12] The sputtering yield is about 1.0 for the incident Pt atoms of 200 eV, Y_s reaches 0.998, 0.78 and 0.774 for the Pt(100) surfaces at 100K, 300K and 500K, respectively. These results imply that the main role of Pt atoms with an energy of 200 eV is to sputter surface atoms. Therefore, the thickness of the thin film cannot increase in this situation.

(iii) The sputtering yields at the substrate temperatures of 100 K, 300 K and 500 K give the same tendency with the change of incident energy, and there is little difference among them.

Figure 3 presents the sputtering pattern for the 200 eV incident atoms on the substrate at 300K. The sputtering pattern is recorded at the plane about 0.6 nm from the surface of the substrate. We can see clearly that it shows a symmetric pattern although the incident positions of the incident atoms are randomly chosen within one cell. The symmetric pattern is a reflection of the crystal symmetry and has been confirmed in many experiments.

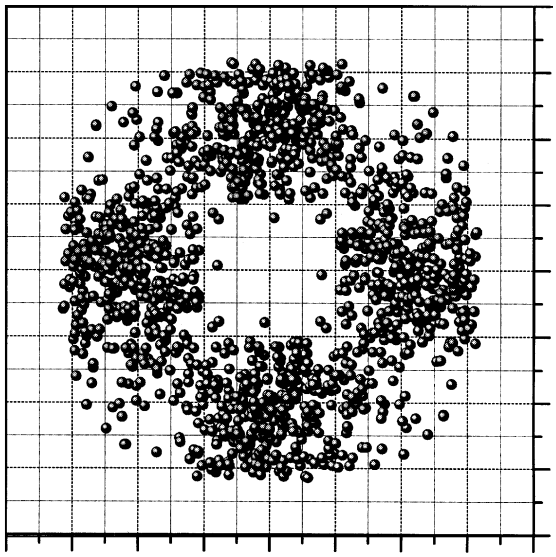


Fig.3. Sputtering pattern of Pt atoms impacting on a Pt(100) surface: T_{sub}=300 K; E_{inc}=200 eV; 500 runs are performed.

C. Adatom yields

Adatom yields resulting from the incident atom dominate the processes of nucleation and growth mode in the film synthesis. As observed in experiments, energetic ions can promote nucleation in the early stage of film growth[13] and change the preferred growth orientation of the films.[14] However, adatom yields cannot be easily measured accurately in experiments. Especially in the situation when the incident atoms are the same as the substrate or film atoms, we cannot distinguish the contribution of the incident atom from that of the substrate or the film. Therefore, computer simulation is needed to reveal the physical mechanism in the adatom generation due to the incident atoms.

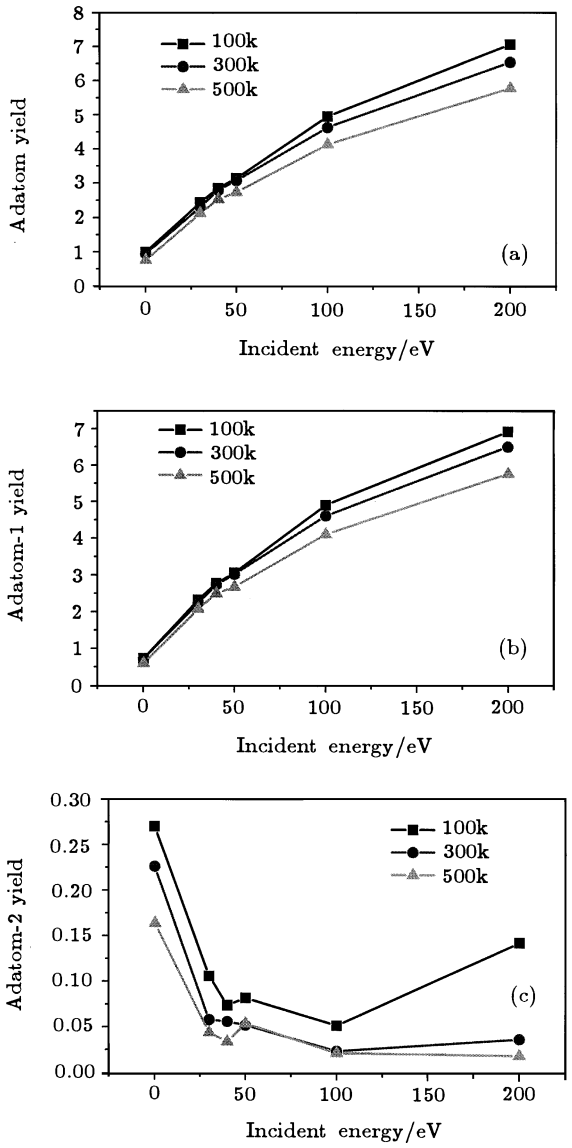


Fig.4. Adatom yields of incident Pt atoms with 0.1eV to 200eV on Pt(100) surfaces. The substrate temperatures are 100K, 300K and 500K: (a) the whole adatom yields; (b) the adatom yields which come from the substrate atoms; and (c) the adatom yields which come from the incident atoms.

Figure 4 presents the adatom yields (Y_a) obtained in the simulations of the incident atoms, with energies ranging from 0.1eV to 200eV, impacting on the substrate surface at temperatures of 100 K, 300 K and 500 K. Figure 4(a) is the total adatom yield produced by incident atoms. Figures 4(b) and 4(c) are the figure contributions of substrate atoms and incident atoms to the adatom yield, respectively. In this paper, we define the adatom coming from the substrate as adatom-1 and that coming from incident atoms as adatom-2. In Figs.4(a) and 4(b) we can see that the Y_a-data exhibit the following characteristics:

(i) The adatom yields are typically larger than the sputter yields (see also Fig.1), and the adatom yields increase with the incident energy. This is because the threshold energy for generating the adatom is lower than that for generating the sputtering atoms; and the higher the incident energy, the more the atoms can be moved. In other words, the incident atoms with higher energy can transfer more kinetic energy to the substrate atoms than those with lower energy.

(ii) For a fixed incident energy, the higher the substrate temperature, the lower the adatom yield. This can be explained by the incorporation between adatom and vacancy because the diffusion activities of adatom and vacancy at higher temperatures are higher than those at lower temperature. Therefore, the probability of incorporation between adatom and vacancy at higher temperatures is larger than that at lower temperature.

(iii) The tendency of the increase of adatom-1 yields with the increase of energy is the similar to that in Fig.4(a), and the values are in the same range. So we can conclude the substrate atoms are the main source of the adatom.

Figure 4(c) presents the adatom yields contributed by the incident atoms, or the incident atoms become adatoms after they impact on the substrate. In general, the adatom-2 yields decrease with the increase of incident energy although fluctuation exists. This is because the higher the incident energy, the deeper the incident atom can penetrate. When the incident atoms penetrate through the surface layer of the substrate, they have a very small probability of returning to the surface due to the energy loss. The fluctuation may come from the statistical errors in the simulation. In Fig.4(c) we can see that the adatom-2 yields are much lower than the adatom-1 yields. When the incident energy is 0.1eV (about equal to the energy of the incident atom in vapour deposition), the adatom-2 yields are the highest, being in the range of 0.17–0.27. This means that the incident atoms have a very small probability of becoming adatoms even if no additional energy is applied to the incident atom. It is surprising that the adatom-2 yields at higher temperatures are also lower than those at lower temperatures. We can also see that the adatom-2 yields decrease very fast when the incident energy is below the sputtering threshold. When the incident energy is higher than the sputtering threshold, the adatom-2 yields decrease slowly with the increase of incident energy. This can be explained as: when the incident energy is lower than the sputtering threshold, the energy of incident

atoms is mainly transferred to the atoms in the surface layer, and the incident atoms have a probability of moving on the surface. When the incident energy is higher than the sputtering threshold, the incident atoms have a large probability of penetrating through the first layer of the substrate. So the adatom-2 yields are low at high incident energies.

D. Vacancy yields

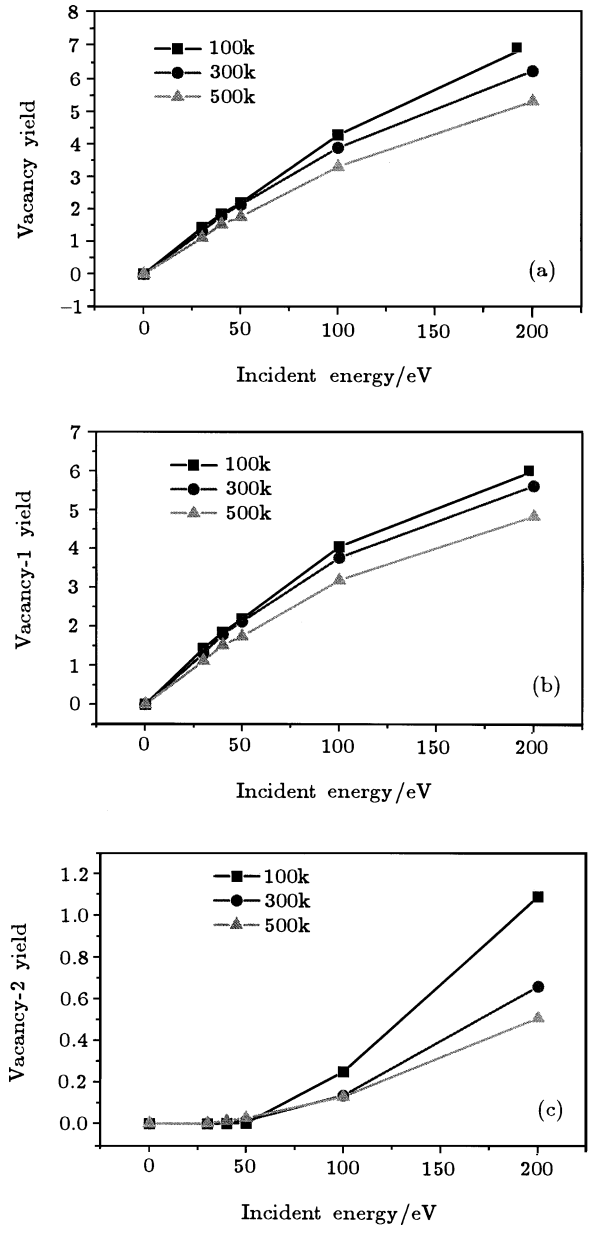


Fig.5. Vacancy yields of incident Pt atoms with 0.1eV to 200eV deposited on Pt(100) surfaces. The substrate temperatures are 100K, 300K and 500K: (a) the whole vacancy yields; (b) the vacancy yields in the first layer; and (c) the vacancy yields in the second layer.

Figure 5 presents the vacancy yields (Y_v) obtained in the simulations of the incident atoms with energies ranging from 0.1–200eV, which impact on the substrate surface at temperatures of 100 K, 300 K and 500 K. Figure 5(a) is the total vacancy yield produced by the incident atoms. Figures 5(b) and 5(c) are the vacancy yields in the first and second layers, respectively. We call the vacancy yields in the first and the second layers, the vacancy-1 and vacancy-2 yields, respectively. In the figure we can see that the vacancy yields increase with the increase of incident energy and decrease with the increase of substrate temperature. The results can also be explained by using the energy transfer and incorporation between the adatom and vacancy, as in the description given above. The increase tendency of vacancy yields with the increase of incident energy in Figs.5(a) and 5(b) is similar to that of adatom yields in Figs.4(a) and 4(b). The vacancy yields in the second layer, however, increase with the increase of incident energy faster than those in the first layer when the incident energy is higher than the sputtering threshold. Below the sputtering threshold, small vacancies in the second layer can be generated. This result also confirms the conclusion that the incident atoms mainly transfer their kinetic energy to the atoms in the surface layer when the incident energy is lower than the sputtering threshold. When the incident energy is higher than the sputtering threshold, incident atoms can penetrate through the surface layer and damage the crystal lattice below the surface layer.

E. Discussion

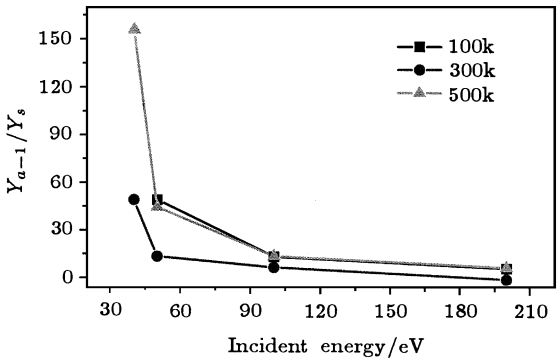


Fig.6. Ratio of the adatom-1 yield to the sputtering yield for the incident energy higher than the sputtering threshold.

In their experiment[3] Michely and Teichert observed that the value of Y_a/Y_s does not satisfy the prediction by using linear cascade theory, in which a ratio $Y_a/Y_s \approx 1$ is obtained for the whole range of incident energies. They found the ratio Y_a/Y_s=8.9 for the

case of 40 eV Xe ions impacting on the Pt(111) surface. Figure 6 shows the ratio of the adatom-1 yield to the sputtering yield for incident energies higher than the sputtering threshold. In the figure, we can see that the ratio Y_a/Y_s is much larger than 1, and the ratios decrease with the increase of incident energy. This result is qualitatively similar to Michely and Teichert's result, but differs from the molecular dynamics simulation of Ar ion bombardment on Cu(100) obtained by Webb and Harrison,[1] where $Y_a/Y_s \approx 1$ for energies greater than 1 keV and a tendency for $Y_a/Y_s < 1$ for energies smaller than 1 keV.

TRIM is a famous Monte Carlo code usually used in the simulations of sputtering and vacancy yields, but it is not very suitable for the case of very low incident energy. Table I shows the sputtering, backscattering and vacancy yields obtained by MD simulation and TRIM. We can see that the sputtering and backscattering yields obtained by using TRIM are similar to those calculated by the MD simulation. The vacancy yields in the MD simulation, however, are much higher than those calculated by TRIM. This is because the TRIM calculation is based on the binary collision approach theory, which cannot describe the interaction between atoms when the incident energy is very low. TRIM calculations performed for various ion species and energies give the same results: about half of the atoms approaching the surface are sputtered, i.e., $Y_a/Y_s \approx 1$.

Table 1. The sputtering, backscattering and vacancy yields obtained by TRIM and MD simulation.

$E_{\rm inc}$(eV)	Y_s(MD)	Y_s(TRIM)	Y_b(MD)	Y_b(TRIM)	Y_v(MD)	Y_v(TRIM)
50	0.062	0.053	0	0.011	2.129	0.8
100	0.36	0.217	0.006	0.026	4.304	1.5
200	0.998	0.5807	0.086	0.039	7.124	3.1

IV. CONCLUSION

The molecular dynamics simulations of the incident Pt atoms with low energy, which impact on the Pt(100) surface, show that:

(1) There is a sputtering threshold for the incident energy, below which no surface atoms can be sputtered. When the incident energy is higher than the sputtering threshold, the sputtering yield increases with the incident energy. For the incident energy of 200 eV, the sputtering yields are about 1.0.

(2) The adatom and vacancy yields increase as the incident energy increases. The ratio Y_a/Y_s is similar to the observation in the experiment and much higher than the results predicted by linear cascade theory and TRIM calculation.

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