Estimation of the Pressure-Distance Product for Thermalization in Sputtering for Some Selected Metal Atoms by Monte Carlo Simulation

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Abstract

We propose a method to obtain the pressure-distance product (*pd*) for thermalization in the sputtering process using a Monte Carlo (MC) simulation. Sputter-ejected atoms proceed forward with high energy, and fall into random motion finally. That is, after many MC trials the "average position" of atoms reaches saturation. The thermalization distance *d* can be estimated from this saturation position. We could obtain the *pd* product for Al, Cu, and Mo in argon atmosphere. The *pd* values agreed well with the pressure dependence of the deposition profile observed experimentally.

In sputter deposition, the transport process of sputtered atoms from the target to the substrate is known to be strongly affected by gas pressure[1]. Initially, sputtered atoms have energy on the order of 1-10 eV[2], which is much greater than the kinetic energy of ambient gas atoms and molecules. At low gas pressures, sputtered atoms experience few collisions before they arrive at the substrate, so they retain their high energy throughout the transport process. On the other hand, when gas pressure is high, sputtered atoms are decelerated many times by collisions with ambient gases until their speed distribution reaches an equilibrium with the gases. This process is called "thermalization" of sputtered atoms. The transport modes before and after thermalization are often called "ballistic" and "diffusive", respectively, and the mode transition caused by gas pressure gradually changes the deposition rate and the thickness profile of the sputter deposition process. Gas pressure is also known to affect strongly on the microstructure of sputtered films[3] because the energetic bombardment onto growing films[4,5], significant in the ballistic transport regime, is lost upon thermalization.

Thermalization is dominated by the amount of collision with gas atoms. Therefore, the product of the gas pressure and the thermalization distance, called the "*pd* product," should be a specific value for sputtered atoms of a given element. This concept was discussed by Keller and Simons in their theoretical consideration[6], and it motivated the development of the Monte Carlo (MC) simulation of the particle transport process in its early years[7–10]. A state-of-the-art MC simulation can be found in the review by Depla and Leroy[11].

The *pd* product is dependent on the target materials because the atomic size and mass affect the

collision and scattering processes. The difference in the *pd* product between elements of different atomic mass was reported to be the origin of the compositional difference between sputtered films and alloy targets such as AlCu and TiW[12]. If it is possible to obtain a direct measurement of the *pd* product for various elements, such a method would be useful to the sputter deposition community.

In a previous study[13], we experimentally evaluated the pressure dependence of the thickness profile in sputter deposition with three types of metal targets (Al, Cu, and Mo) with different atomic mass. We prepared a holder equipped with three quartz crystal microbalance monitors (QCMs). Two QCMs were facing the target - on the "confronted" face - and the third was located on the back face which was hidden from the target. The holder was located 4 and 6 cm away from the target, and the pressure dependence of the deposition rates was measured. On the confronted face, the deposition rate and the thickness uniformity were almost unchanged at lower gas pressures. However, the deposition rates decreased and the thickness uniformity worsened with increasing the gas pressure beyond a certain value. The transition occurred at around 1–5 Pa. On the hidden face QCM, the deposition reached its maximum at a gas pressure of 1–2 Pa. Both the transition pressure on the confronted face and the peak pressure on the back face were lower for lighter elements. Our MC simulation could well explain these experimental results. Especially the deposition rate peak on the back face was reproduced quantitatively both in height and gas pressure. The experimentally observed phenomena could be ascribed to the thermalization of the sputtered atoms, and the lighter elements were expected to have a smaller *pd* product value.

In this work, we propose a method to obtain the *pd* product by developing our Monte Carlo simulation. The model takes the ambient Ar gas motion into account[14] and can handle the thermalization of sputtered atoms seamlessly. Because of their high initial kinetic energy, sputtered atoms are expected to proceed forward. After thermalization, however, they diffuse isotropically. Hence, if we trace many atoms with MC trials and average their position, the "center-of-mass" (COM) of the atoms may reach saturation with time. By multiplying the distance by the ambient gas pressure, we can determine the thermalization *pd* product. We applied this idea to Al, Cu, and Mo transport in an Ar atmosphere and obtained the resulting *pd* product values.

The MC framework was the same as in the previous study[13]. A full description of the simulation is provided in one of the author's doctoral dissertation[15]. The scattering between the sputtered atoms by Ar gas atoms was treated with Born-Meyer type interatomic potential with parameters given by Abrahamson[16]. The ambient Ar gas pressure was varied between 1 and 10 Pa, and the gas temperature was assumed to be 350 K. Atoms were injected into the free volume from the origin along the z axis and their motion, including the free flight and collision/scattering with argon, was recorded. Typically, 10^6 atoms were traced and processed in each condition.

To illustrate the behavior of sputtered atoms, we applied the MC code for a single initial energy case. Figure 1 shows the simulation snapshots of real and velocity spaces for copper atoms with 5 eV of initial kinetic energy (which corresponds to a speed of 3900 m/s) in argon of 5 Pa and 350 K. As shown in Fig. 1 (left), the atoms started at the origin at $t = 0$, proceeded in the $z > 0$ direction in the 20 μs

snapshot, and diffused isotropically after that. At the Fig. 1 (right), it is also shown that the copper atoms were decelerated and came to have an isotropic velocity distribution as time proceeds. Figure 2 shows the time dependence of the *z* component of the COM (a) and the time evolution of the speed distribution of copper atoms (b). It shows clearly that the distance of the averaged position from the origin saturates at around 50 μs. At that time, the speed distribution becomes Maxwellian, which indicates the thermalization of the atoms. The *x* and *y* components of the atoms' COM were zero within the MC randomness.

In the actual calculation of the *pd* products of metals, we determined the initial energy of atoms by utilizing Thomson's energy distribution formula[17], which describes the energy distribution of atoms sputtered from a solid surface. The binding energy of the target material, a parameter of the formula, was assumed to be 3.39, 3.49, and 6.82 eV for Al, Cu, and Mo, respectively; these values were used in the work by Yamamura and Tawara[18]. The primary (Ar) ion energy, another parameter in the formula, was assumed to be 400 eV. The gas temperature was assumed to be 350 K.

Figure 3 shows the pressure dependence of the saturation distance of Al, Cu, and Mo. As expected, the distance was inversely proportional to the gas pressure, and the *pd* products were found to be 7.1, 10.0, and 14.3 Pa cm for Al, Cu, and Mo, respectively. These values are on the same order with those reported in previous studies; Keller and Simmons reported 8 Pa cm for Si by fitting their theoretical formula to the experimentally obtained deposition rate[6]. The previous MC works[7–10] did not directly present a specific *pd* value for each case, but showed their calculation results as *pd* dependence of the

average energy (or the energy distribution) of sputtered atoms. The *pd* at which the prominent deceleration of sputtered atoms occurred was around 10 Pa cm in their calculation.

Comparing our MC values with the experimental results[13] described earlier, it is reasonable that the transitions caused by the thermalization occurred at gas pressures of 1–5 Pa, where the target-to-substrate distance was 4–6 cm. The *pd* product in this study was smaller for lighter elements. In ballistic mode transport, where gas motion is negligible, atoms much heavier than gases are considered to go further since they lose less kinetic energy in binary collisions. Light atoms also lose less energy in collisions, but the backscattering of the atoms of such element by gases is more effective on the reduction of the *pd* product.

The thermalization distance d is greater than the collision mean free path (MFP) λ, because sputtered atoms do not completely lose their energy and forward momentum by a single collision event. High energy atoms, such as sputtered atoms from the target, tend to have longer MFP because of the less effect of ambient gas motion[19] and of effectively smaller cross section of the potential scattering[11]. The "$p\lambda$" can be calculated to be 0.8~1.7 Pa cm by applying energy dependent cross sections (see discussion by Somekh[7] for example). Therefore, sputtered atoms are considered to experience several to 10 times of collisions before thermalization.

It should be noted that the obtained *pd* product is sensitive to the gas temperature. As a matter of fact, when we assumed the gas temperature to be 400 K, the calculated *pd* product increased by ~14% in comparison to the 350 K case. In actual sputter deposition, it is known that the gas density reduction

occurs locally due to heat flux from the target ("sputtering wind")[20,21]. This is prominent at higher gas pressures, so that slightly greater *pd* values should be employed in such situations.

In summary, we have developed a method to calculate the thermalization *pd* product in the sputter deposition process using an MC framework where the thermal motion of gases is properly taken into consideration. We obtained results of 7.1, 10.0, and 14.3 Pa cm for Al, Cu, and Mo, respectively, in the case of Ar gas at a temperature of 350 K. The obtained values agree well with results from our previous experiment in explaining the transition gas pressures and their element dependence.

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Figure Captions

Fig. 1: The evolution of Cu atoms injected into the volume along the z axis at $t = 0$ with 5 eV of energy. The argon gas pressure and temperature in the volume were 5 Pa and 350 K, respectively. Snapshots of 5000 atoms in real space (left) and in velocity space (right) are given.

Fig. 2: (a) The time dependence of the z component of the "center-of-mass" of Cu atoms which were injected into the volume under the same conditions as in Fig. 1 (Cu initial energy: 5 eV, Ar gas pressure: 5 Pa, gas temperature: 350 K). The saturation length at longer periods is considered to give the thermalization distance. (b) The speed distribution of the Cu atoms. The black line denotes the Maxwellian for Cu vapor at 350 K.

Fig. 3: Gas pressure dependence of the thermalization distance of Al, Cu, and Mo atoms. The Ar gas temperature was 350 K, and the initial energy of the injected atoms was in accordance with the Thompson's formula with a primary ion energy of 400 eV.

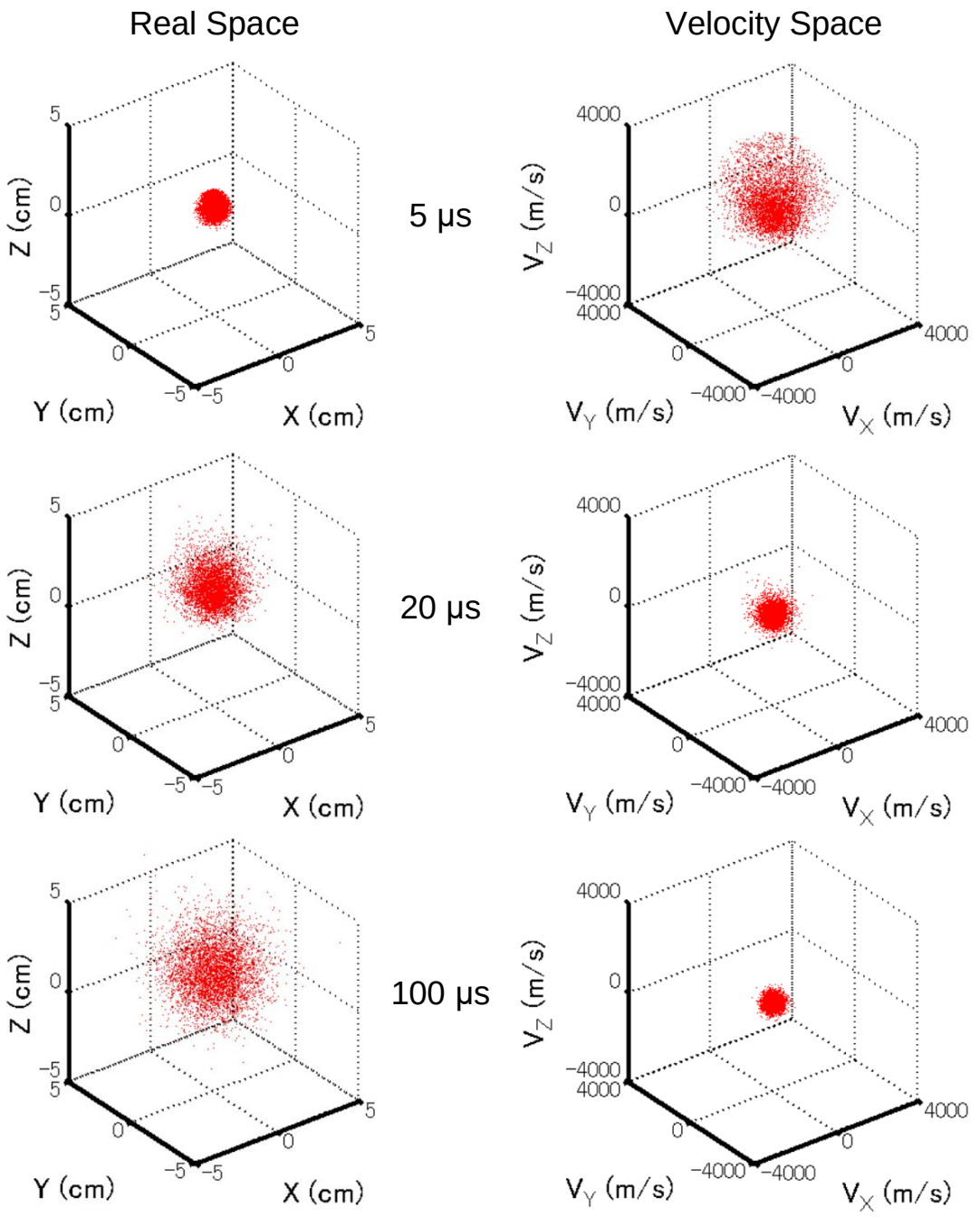
Real Space
Velocity Space
5 μs
20 μs
100 μs
Z (cm)
Y (cm)
X (cm)
V_Z (m/s)
V_Y (m/s)
V_X (m/s)
5
0
−5
4000
−4000

Fig. 1

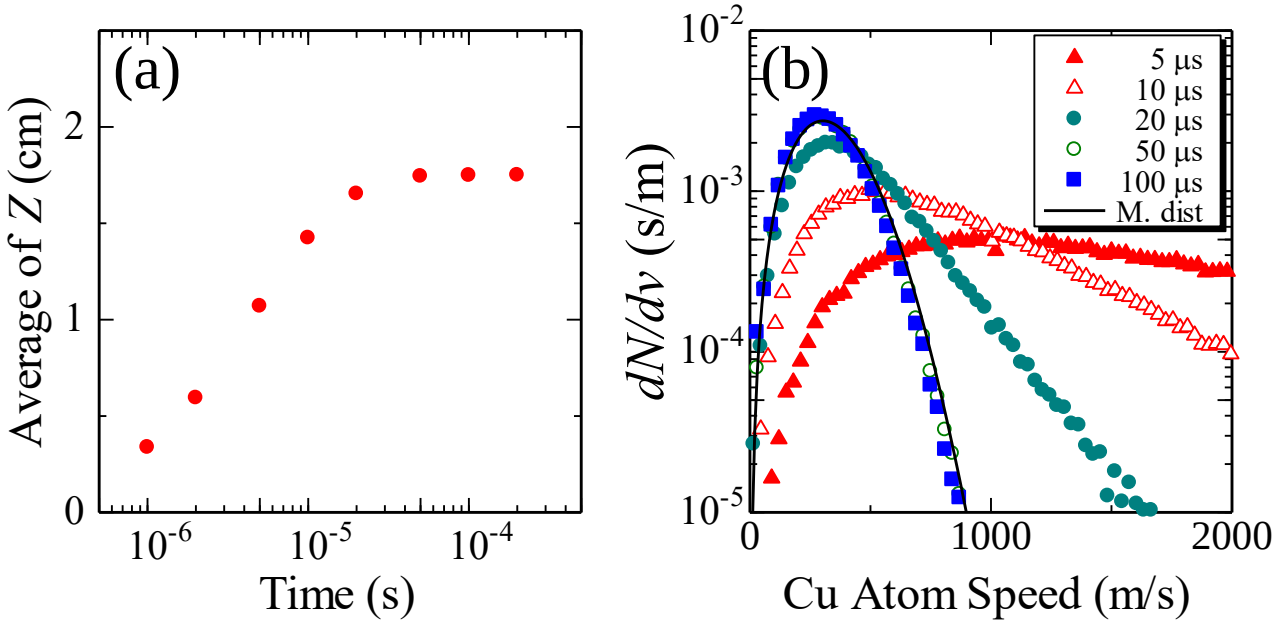
(a)
Average of Z (cm)
0
1
2
10-6
10-5
10-4
Time (s)
(b)
dN/dv (s/m)
10-2
10-3
10-4
10-5
0
1000
2000
Cu Atom Speed (m/s)
5 μs
10 μs
20 μs
50 μs
100 μs
M. dist

Fig. 2

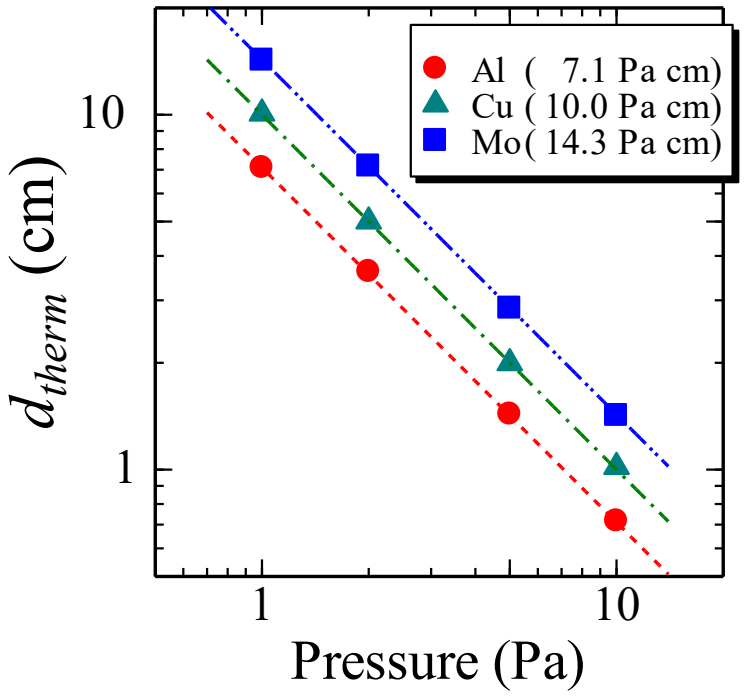
Al (7.1 Pa cm)
Cu (10.0 Pa cm)
Mo(14.3 Pa cm)
10
1
1
10
d_{therm} (cm)
Pressure (Pa)

Fig. 3