



Title	Molecular Dynamics simulations of surface atomic processes in ion-beam and plasma etching
Author(s)	Mauchamp, Aini Nicolas
Citation	大阪大学, 2022, 博士論文
Version Type	VoR
URL	https://doi.org/10.18910/89620
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Doctoral Dissertation

Molecular Dynamics simulations of surface atomic processes in ion-beam and plasma etching

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June 2022



Graduate School of Engineering

OSAKA UNIVERSITY

Acknowledgment

I would like to express my thanks to all people who helped me during my Ph.D. at Osaka University and my stay in Japan.

I am very grateful to Prof. Satoshi Hamaguchi, my Ph.D. supervisor for this opportunity to come to Japan to do my Ph.D. His vast knowledge, experience and endless support were very helpful. Completing my Ph.D. without his help would not have been possible.

I am also very grateful to Michiro Isobe for its help for numerical simulations and for the setup of the computation system used to perform numerical simulations. Discussions about various numerical related subjects were also very enjoyable.

I also thank all members of Hamaguchi Lab, staff, students, Japanese or not, past or present. All of them were of great help and made my stay even more agreeable.

Finally, I thank my family for their support during these years so far from home.

Abstract

Over the last century, thanks to the constant improvement of manufacturing techniques, the typical sizes of semiconductor devices steadily decreased to reach atomic scales. At such small scales, further size reducing becomes very challenging and expensive. As traditional planar structures were reaching their scaling limits, device structures shifted from planar structures to three-dimensional (3D) structures such as FinFET, while layers of semiconductor devices are vertically stacked in skyscraper-like structures to increase device density as in 3D NANDs memories. In parallel, the development of new devices, such as MRAMs memories, requires the use of new materials which require the use of new processing techniques.

Plasma etching processes are widely used in semiconductor device manufacturing. It consists in removing atoms from the material surface by bombarding it with incident particles, typically ions and radicals. Surface atoms are removed from the material surface either physically, i.e., from the collision cascade induced by the impact, or chemically, i.e., from the bond formation between injected particles and surface atoms.

The numerous theoretical and experimental studies on sputtering contributed to a better understanding of the sputtering mechanisms. However, none of these studies give a comprehensive understanding of the etching mechanisms and of its dependency on physical quantities such as the incident energy or the atomic mass.

In this thesis, the physical etching of a material surface is studied using molecular dynamics (MD) simulations, to obtain a better understanding of the sputtering mechanisms dependency on physical parameters.

Physical sputtering was first studied for a LJ solid, i.e., for a material made of atoms interacting through a Lennard-Jones (LJ) potential function, a simple

two-body potential function which depends on two parameters ε and σ . When the incident particles are of the same species as the material atoms, i.e., for self-sputtering, all interactions were represented by the same LJ potential function. The physical sputtering yield was found to be a function of the normalized incident energy $\mathcal{E}$, defined as the ratio of the incident energy to the LJ parameter ε , and of the incident angle α . The comparison of the obtained physical self-sputtering yields with experimental self-sputtering yields for several materials showed a good agreement at low incident energies. At large incident energies, obtained yields are deviating from experimental yield due to the inaccuracy of the LJ potential function at low interatomic distances. It was also shown that the modification of LJ potential function at low interatomic distances allows to obtain a better agreement with experimental yields for large incident energies. When the incident particles and material atoms are of the different species, i.e., for sputtering, interactions were represented used two different LJ potential functions. Interaction between material atoms were represented using a LJ potential function, while interactions with injected particles were represented using a repulsive LJ potential function. On top of the dependency on the normalized incident energy $\mathcal{E}$ and the incident angle α , the physical sputtering yield Y was then found to depend on two additional parameters, the ratio of the masses μ and the relative interaction range ρ . The mass ratio μ is defined, as its name implies, as the ration of the incident particle mass to the material atom mass, whereas the relative interaction range ρ is defined as the ratio of the repulsive LJ parameters to the LJ parameters . For real materials, these two parameters μ and ρ were found to be related and to vary within a narrow range. Within the range, the sputtering yield varied by a factor 2 or so, which accounts for the similarity of the experimentally observed physical sputtering yield for different incident particles.

The physical sputtering yield Y was then evaluated for the self-sputtering of a nickel (Ni) solid using several interatomic potential models based on the embedded atom method (EAM). These potential models were obtained by modifying the low interatomic distance part of existing EAM potential functions designed for Ni bulk. It was found that, although each of the potential models was accurately reproducing some Ni mechanical properties, the self-sputtering yield was quite different according to the used interatomic potential model at large incident energies.

At low incident energies, the self-sputtering yields obtained with the different potential models showed good agreement with experimental Ni self-sputtering yields.

In the last part, trench etching of Si surfaces covered with SiO₂ hard masks is studied for Cl ion beam etching (IBE) and Cl-based reactive ion etching (RIE) with a flux ratio Cl radicals to Cl⁺ ions of 10. In IBE, 100 eV Cl⁺ ions were injected at normal incidence. In RIE, alongside with Cl⁺ ions, Cl radicals were simultaneously injected with a kinetic energy close to their thermal energy at random incidence angle. The flux ratio of Cl radicals to Cl⁺ ions was set to 10. The etching properties of Si and SiO₂ surfaces were first studied for both IBE and RIE. It was found that, although their sputtering yield are very different, their etch rate are similar due to the much lower Si density in SiO₂. Trench etching of Si surfaces was then studied for both IBE and RIE. The trench profile was found to be quite different for IBE and RIE. For IBE, the etched trench was found to be tapered with an etching more pronounced near the trench centerline. RIE, on the other hand, was found to exhibit a better pattern transfer with a wider and flatter etched profile.

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Introduction

I.1 Background

Over the last century, thanks to the constant improvement of manufacturing techniques, the number of semiconductor devices contained in a single integrated circuit (IC) chip steadily increased as the typical size of semiconductor devices steadily decreased. In 1965, Moore predicted that the transistor density, i.e., the number of transistor per IC chip, will double every two years.¹ This prediction, known as the Moore's law, remains valid until nowadays, although keeping pace with it becomes more and more difficult and expensive due to technological limitations.

As the typical sizes of semiconductor decreased and are nowadays reaching atomic scales (nm-Å), further size reduction becomes very challenging and the traditional planar structures are reaching scaling limits. To further increase the semiconductor device density, transistor structures shifted from planar structures to three-dimensional (3D) structures, such as fin field-effect transistors² (FinFETs) where the gate is surrounding the channel instead of being on top of it as in traditional planar transistors (Fig. I-1). Another technique to increase device density is to stack multiple layers of semiconductor devices on top of each other to form skyscraper-like structures. Such techniques are used, for example, in 3D NANDs memories^{3,4} (Fig. I-2a) where multiple layers of memory cells are stacked

on top of each other. Currently, 3D NANDs are made of around 40 layers and more layers will be used in the future to reach higher cell density.

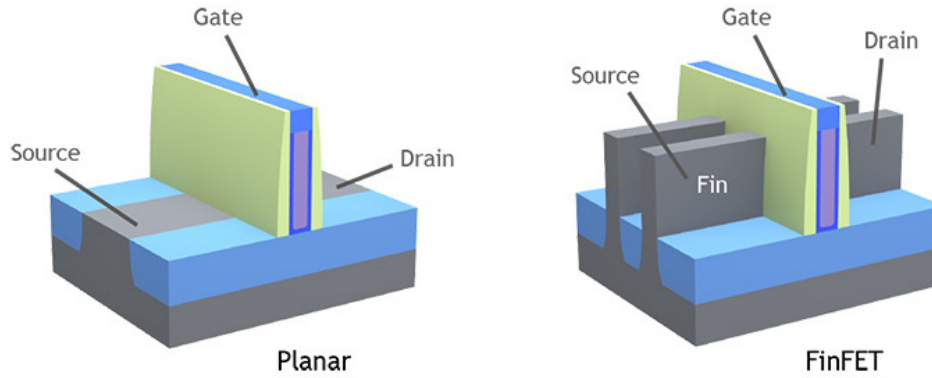
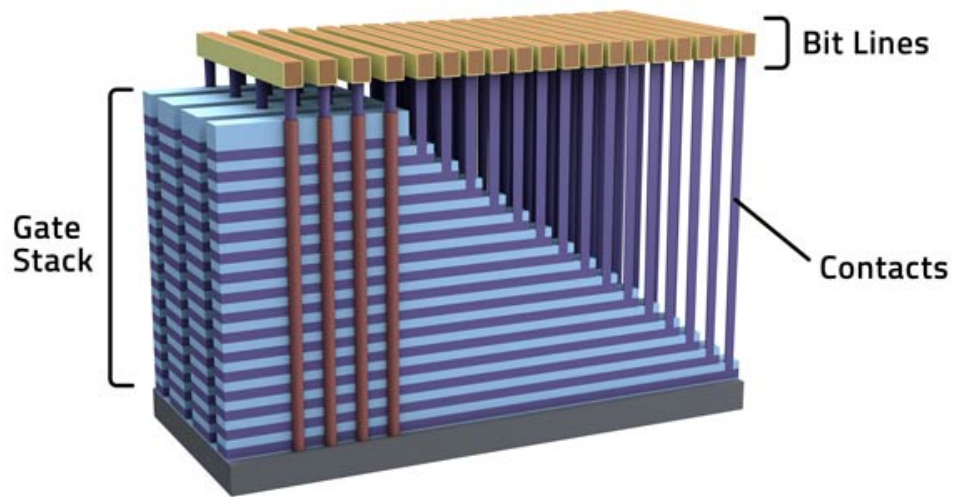


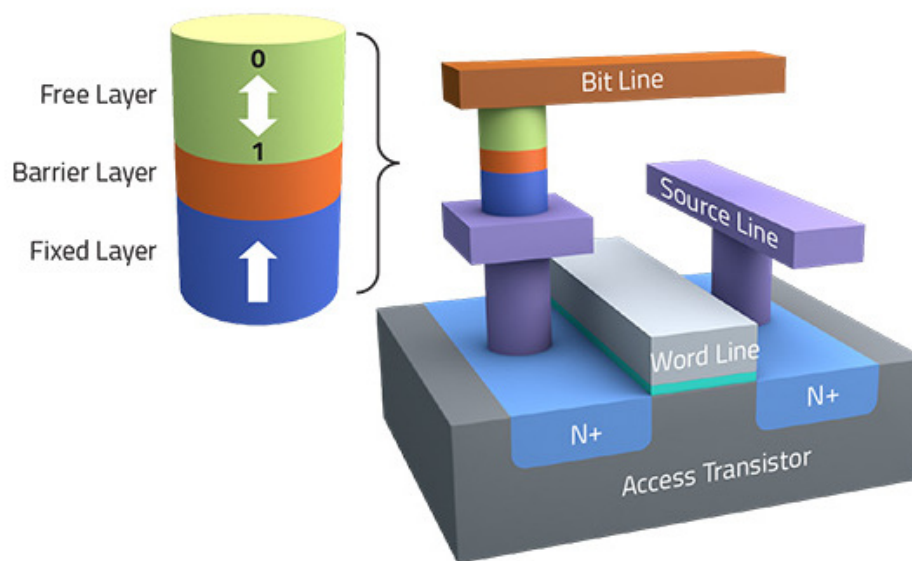
Figure I-1 – Representation of a planar transistor (left) and a FinFET (right).² In the planar transistor, the gate is located on top of the channel between the source and the drain, whereas in the FinFET, the gate is surrounding the channel.

In parallel, the development of new semiconductor devices requires the use of new materials and, therefore, of new manufacturing processes. For example, magnetoresistive random access memories⁵ (MRAMs) (Fig. I-2b) are a new type of non-volatile memory where data are stored using magnetic elements rather than electric elements as in NANDs memories. Therefore, MRAMs requires the use of materials able to keep their magnetic properties, i.e., ferromagnetic material such as iron (Fe), nickel (Ni) or cobalt-iron-boron (CoFeB) alloys.

Plasma etching processes are widely used in semiconductor device manufacturing and significantly contributed to the miniaturisation of semiconductor devices^{6–10}. It consists in the removal of atoms from the material surface due to the impact of incident particles, typically ions or radicals. Surface atoms can be removed either by physical etching or by chemical etching. Physical etching takes place when atoms are removed due to the collision cascade induced by the incident particle impact. At the impact point, momentum is transferred from the incident particle to the surface atoms and then to the successive neighbour atoms, forming a collision cascade. As the collision cascade unfolds, atoms can be pushed upward with enough energy and leave the material. Chemical etching takes place when atoms are removed by forming chemical compounds with the incident particles.



(a) NAND



(b) MRAM

Figure I-2 – Two types of non-volatile memories: (a) 3D NAND³ and (b) magnetoresistive random access memory (MRAM).⁵ Data are stored using electric elements in 3D NANDs, whereas magnetic elements are used in MRAMs.

Upon impact, injected atoms will chemically interact with surface atoms and form chemical compounds such as SiF_x . These compounds are typically weakly bonded with the material bulk and can easily be removed by following incident particles or, in case of volatile compounds, spontaneously leave by themselves. Typically, physical etching requires the use of relatively high incident energies for enough energy to be transferred to the sputtered atoms to leave the material. On the contrary, chemical etching can take place at low incident energies but requires the incident species to be able to chemically react with the material to etch.

Reactive ion etching¹¹⁻¹³ (RIE) is widely a widely used technique for semiconductor device manufacturing (Fig. I-3). In RIE, chemically reactive ions are bombarding the material surface and chemically react with the material atoms to form chemical compounds. These chemical compounds are weakly bonded with the material bulk and can easily be removed using low energy incident ions, or spontaneously be desorbed in the case of volatile compounds such as SiF_4 . RIE offers good selectivity and, as the incident ions have a high directionality, good anisotropic etching is achieved. This anisotropy can be further enhanced using sidewall passivation.

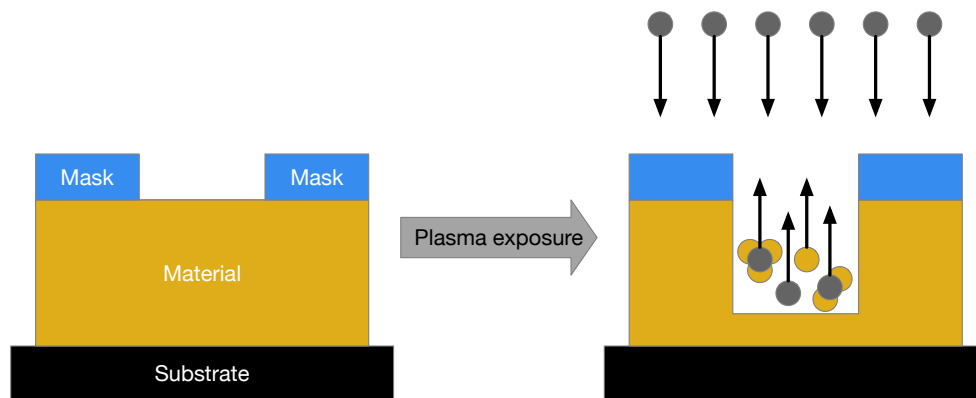


Figure I-3 – Illustration of reactive ion etching (RIE). Incident particles are chemically reacting with the material to form weakly bonded compounds, which are then physically etched. RIE offers a good anisotropy due to the high directionality of the incident ions.

Atomic layer etching^{11,14} (ALE) is an etching technique which offers a precise control on the etching process (Fig. I-4). In ALE, an etching cycle is composed of two distinct steps, the absorption step followed by the desorption step. During the

absorption step, the material surface is exposed to a chemically reactive precursor which will bond with the surface atoms to form a modified layer weakly bonded with the material bulk. Once a single monolayer of precursor is deposited on the material surface, deposition will stop. During the desorption step, the modified layer is physically etching by low incident incident ions. The incident ion energy is set low enough such that once the modified layer is entirely etched, no more etching takes place. ALE is therefore a self-limiting process. At the end of the ALE cycle, a single monolayer has been removed from the material surface. By repeating the ALE cycle as needed, precise etching of the material can be achieved.

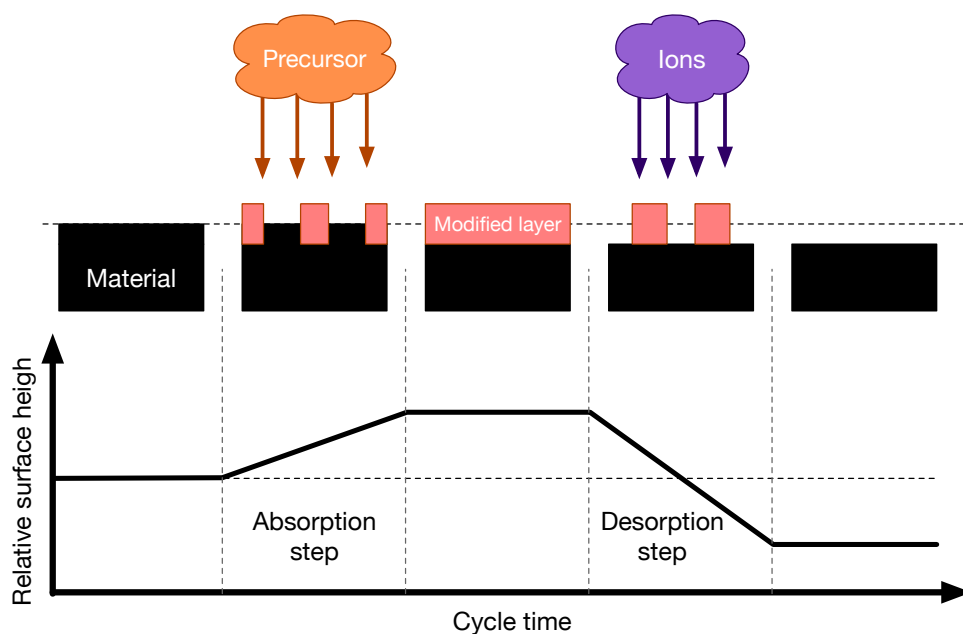


Figure I-4 – Representation of an atomic layer etching (ALE) cycle. An ALE cycle is composed of distinct steps, the absorption step and the desorption step. During the absorption step, the material surface is exposed to a precursor which will chemically interact with the surface to form a modified layer. The modified layer is then physically etched by low energy ions during the desorption step. The precursor is chosen such that it will not interact with the modified layer, hence a single layer of modified layer is formed. Similarly, the ion energy is such that only the modified layer is etched and etching stops once the entire modified layer has been etched. At the end of the ALE cycle, a single monolayer has been removed from the material surface.

Since the first observation of sputtering on 1853 by Grove¹⁵ and the first real-

istic mathematical model by Sigmund¹⁶ in 1969, sputtering have been extensively studied both theoretically and experimentally. These studies contributed to have a better understanding of the sputtering mechanisms. However, none of these studies give a comprehensive understanding of the sputtering mechanisms, sputtering yield and its dependency of physical parameters such the incident energy or atomic mass.

I.2 Sputtering yield

An important parameters in etching processes is the sputtering yield Y which quantifies the rate of atom removal from a material surface exposed to incident particles bombardment. It is defined as the average number of atoms removed from the material surface by a single incident particle. The larger the sputtering yield, the more atoms are removed by a single incident particle. When removed atoms and incident particles are of the same species, the sputtering yield Y also indicates the rate of atom deposition on the surface.

The sputtering yield $Y_{\beta-\alpha}$ of a species α by a species β is given by the ratio of the number $N_{\alpha,\text{Sputtered}}$ of atoms of species α sputtered from the material surface to the number $N_{\beta,\text{Incident}}$ of incident particles of species β :

$$Y_{\beta-\alpha} = \frac{N_{\alpha,\text{Sputtered}}}{N_{\beta,\text{Incident}}}$$

The number of sputtered atoms $N_{\alpha,\text{Sputtered}}$ is calculated by counting the number of atoms $N_{\alpha,\text{Away}}$ of species α going away from the material surface, or by computing the change $\Delta N_{\alpha,\text{Material}}$ of the number of atoms of species α in the material. The sputtering yield $Y_{\beta-\alpha}$ is calculated by either of two definitions:

$$Y_{\text{Away}} = \frac{N_{\alpha,\text{Away}}}{N_{\beta,\text{Incident}}}; \quad Y_{\text{Delta}} = -\frac{\Delta N_{\alpha,\text{Material}}}{N_{\beta,\text{Incident}}}$$

When the sputtering atoms and injected particles are of different species, i.e., $\alpha \neq \beta$, these two definitions of the sputtering yield $Y_{\beta-\alpha}$ are equivalent as any atom of species α going away from the material surface necessarily originates from the material. Therefore,

$$N_{\alpha, \text{Away}} = -\Delta N_{\alpha, \text{Material}} \Rightarrow Y_{\text{Away}} = Y_{\text{Delta}}$$

On the other hand, when sputtering atoms and injected atoms are of the same species, i.e., $\alpha = \beta$, the two definitions are not equivalent. Indeed, as incident and materials are identical and undistinguishable, injected atoms are considered as part of the material once injected. If the number of atoms in the material does not change, i.e., $\Delta N_{\text{Material}} = 0$, then the number of atoms going away from the material is equal to the number of incident atoms, i.e., $N_{\text{Away}} = N_{\text{Incident}}$. Similarly, if no atoms are going away from the material, i.e., $N_{\text{Away}} = 0$, then the number of atoms in the material increased by the number of incident atoms, i.e., $\Delta N_{\text{Material}} = N_{\text{Injected}}$. Therefore,

$$N_{\text{Away}} = -\Delta N_{\text{Material}} + N_{\text{Incident}} \Rightarrow Y_{\text{Away}} = Y_{\text{Delta}} + 1$$

Depending on how $N_{\alpha, \text{Sputtered}}$ is calculated, the obtained self-sputtering yield can vary by ± 1 . It is therefore important to consider how the self-sputtering yield is calculated, especially when compared with experimental yields as the definition of the self-sputtering yield must agree.

I.3 Objectives

The goal of this study is to use MD simulations to investigate the etching of a material by incident particles, ions and radicals. This thesis focuses on the physical sputtering mechanisms and intends to determine its dependency on physical parameters such as the incident particle energy or the atom mass. The rest of this thesis is structured as follows:

In Chap. II, the background of the numerical simulations performed in this thesis is presented. The first part focuses on the description of the used molecular dynamics (MD) simulations. The second part presents the four used interatomic potential functions. The last part of this chapter presents several material properties.

In Chap. III, the physical self-sputtering of a LJ solid is studied. All atoms, material and incident atoms, are identical and are interacting through a single

Lennard-Jones (LJ) potential function. The physical sputtering yield Y is evaluated for a wide range of incident energies to obtain the universal curve of the physical self-sputtering yield as a function of the normalized incident energy $\mathcal{E}$, defined as the ratio of the incident energy to the LJ parameter ε . Obtained self-sputtering yields are then compared to experimental self-sputtering for several materials and show a good agreement for low incident energies. The agreement for large incident energies is improved by modifying the repulsive part of the LJ potential function.

This study is extended in Chap. IV to incident particles and material atoms of different species. More specifically, the interest of this chapter is to unveil the reason behind the similarity of experimental physical sputtering yield for incident ions of different masses. Interactions between material atoms are represented by a LJ potential function, whereas interactions with incident particles are represented by a repulsive LJ potential function. The sputtering yield depends then on two additional parameters, the ratio of the masses μ and the relative interaction range ρ . The mass ratio μ is defined, as its name implies, as the ratio of the incident particle mass to the material atom mass, whereas the relative interaction range ρ is defined as the ratio of the repulsive LJ parameters to the LJ parameters, respectively. The physical sputtering yield Y is evaluated for a range of incident energies $\mathcal{E}$, mass ratio μ and relative interaction range ρ to obtain the dependency of the physical sputtering yield. For actual materials, the mass ratio μ and the relative interaction range ρ is found to be related and to vary within a narrow range. The comparison with experimental sputtering yields shows a good agreement.

In Chap. V, the physical self-sputtering is studied for a specific material, nickel (Ni), using the embedded atom method (EAM) potential function, a popular potential function for metallic systems. The physical sputtering yield Y is evaluated for a range of incident energies up to a few thousands eV and for several potential models. These potential models are based on existing EAM potential functions for Ni and were designed to accurately reproduce mechanical properties of bulk Ni. Comparison of the obtained self-sputtering yields with experimental yields for Ni self-sputtering shows that the used potential model plays an important role in the evaluation of the self-sputtering, especially at high incident energies.

In Chap. VI, trench etching of Si surfaces covered with SiO₂ hard masks is

studied for Cl^+ ion beam etching (IBE) and Cl-based reactive ion etching (RIE). In IBE, 100 eV Cl^+ ions are injected at normal incidence. In RIE, alongside with Cl^+ ions, Cl radicals are simultaneously injected with a kinetic energy close to their thermal energy at random incidence angle, with a flux ratio of Cl radicals to Cl^+ ions of 10. The etching of Si and SiO_2 surfaces is first studied to determine their etching properties for both IBE and RIE. Trench etching of Si surfaces for IBE and RIE is then studied. The trench profile for IBE and RIE are found to be quite different. RIE exhibits better pattern transfer than IBE.

The conclusions are given in Chap. VII and are followed by three appendices.

In Append. A, the derivation of the integration algorithm used for the numerical simulations, the velocity-Verlet algorithm, from the Verlet algorithm is given. These two integration algorithms are mathematically equivalent but numerically different.

The Append. B shows the calculation of two material properties, the lattice constant l_a and the cohesive energy E_C , in the case of a material having an fcc crystalline structure and made of atoms interacting through a LJ potential function. In this case, the two material properties can be evaluated from the parameters ε and σ of the LJ potential function.

The Append. C gives an extension of the study performed in Chap. IV to a full LJ system, where all interactions are represented by a LJ potential function. The physical sputtering yield then depends on additional parameters.



Molecular Dynamics simulations

Physical phenomena have been investigated by humanity since the ancient times to be able to understand, control, reproduce and predict them. The first investigations were performed by simply observing the phenomena themselves in the nature. Later, theoretical models were established based on these observations to quantify the phenomena using mathematical expressions, models which are solved to explain and predict observations. This combination of observations (experimental studies) and predictions (theoretical studies) allowed to understand numerous physical phenomena and led the development of computers in the second half of the twentieth century. The use of computers, and their fast increase in computation power, allow to solve the theoretical models for conditions which were previously too complex. It is, for example, the case of this thesis interest where the position and velocity of thousands of atoms interacting need to be computed millions of times. As the computation power of computers is increasing, more and more complex systems can be simulated.

Numerical simulations are nowadays widely used in most, if not all, domains to investigate physical phenomena by numerically solving theoretical models and comparing the obtain results with experimental results when available. Once the numerical simulations are considered accurate enough to describe the observed phenomena, they can be used to predict experimental results and define the direction experiments should take. The principle of numerical simulations is to compute

the time evolution of a set of variables X whose dynamic is governed by a set of equations $\mathcal{F}$ (Eq. (II-1)). The set of variables X and equations $\mathcal{F}$ are defined by the chosen theoretical model.

$$X_{t+1} = \mathcal{F}(X_{t-N}, \dots, X_{t-1}, X_t, X_{t+1}, \dots, X_{t+N}) \quad (\text{II-1})$$

Once the theoretical model, that is the set of equations, to solve is chosen, it is necessary to define the various parameters needed to perform the simulation. These parameters include both physical parameters, such as atomic masses, and parameters specific to numerical simulations, such as the integration timestep.

In this chapter, I first discuss in Sect. II.1 a key element of all numerical simulations, the integration algorithm. I then present Molecular Dynamics (MD) simulations in Sect. II.2 and the potential functions used in Sect. II.3. Finally, Sect. II.4 presents different computed mechanical properties.

II.1 Integration algorithms

Numerical simulations consist in numerically solving a set of equations $\mathcal{F}$ to obtain the time evolution of a set of variable X . The calculation is performed at distinct values of the time t_n separated by a timestep Δt : $t_{n+1} = t_n + \Delta t$, where n is the step number. Depending on the case, Δt can be constant or change over time. A variable timestep Δt can be useful to optimize the calculation time by increasing it during slow dynamics and reducing it during fast dynamics.

The timestep Δt is an important parameter as it defines how often the integration is performed and is directly correlated to the algorithm accuracy, i.e., how close the calculated values are from the analytic one. Ideally, it should be infinitely small to obtain the best accuracy, but it would make the calculation time infinitely large. Generally, the timestep Δt is chosen large enough to keep the calculation time reasonable, but small enough such that changes in the system during a time Δt are smaller than the typical scales of the system, such as the interatomic distance. Another important point is the algorithm stability, i.e., how a small variation in the initial conditions affects the final results. Typically, algorithms have a range of values of Δt for which they are stable, i.e., a small variation

in the initial conditions has little effect on the final result. Outside of this range, they are unstable and significant variations in the final result can be observed for small variations of the initial conditions.

To present some of the numerous integration algorithms, let's consider a single moving particle whose position x and velocity v at a time t are given by:

$$x(t) = x_0 + v_0 t + \frac{1}{2} a_0 t^2 + \frac{1}{6} j_0 t^3 + \dots \quad (\text{II-2a})$$

$$v(t) = v_0 + a_0 t + \frac{1}{2} j_0 t^2 + \dots \quad (\text{II-2b})$$

Here, x is the position, v is the velocity, a is the acceleration, j is the generally ignored jerk and t is the time. The subscript 0 denotes the value at $t = 0$.

The position $x_{n+1} = x(t_n + \Delta t)$ and velocity $v_{n+1} = v(t_n + \Delta t)$ at time $t_{n+1} = t_n + \Delta t$ are obtained using an expansion in a Taylor series:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} a_n \Delta t^2 + \frac{1}{6} j_n \Delta t^3 + \mathcal{O}(\Delta t^4) \quad (\text{II-3a})$$

$$v_{n+1} = v_n + a_n \Delta t + \frac{1}{2} j_n \Delta t^2 + \mathcal{O}(\Delta t^3) \quad (\text{II-3b})$$

Euler algorithm The Euler algorithm is the simplest integration algorithm. It consists in keeping the terms of order $\mathcal{O}(\Delta t)$ in Eq. (II-3):

$$x_{n+1} = x_n + v_n \Delta t \quad (\text{II-4a})$$

$$v_{n+1} = v_n + a_n \Delta t \quad (\text{II-4b})$$

The Euler algorithm is a simple and fast algorithm but has a low accuracy as it is a first-order algorithm, i.e., the global error is of the order of Δt , and can frequently be unstable. Better stability is achieved by using the Euler-Cromer algorithm presented below.

Euler-Cromer algorithm The Euler-Cromer algorithm, also called semi-implicit Euler algorithm or semi-explicit Euler algorithm, differs from the Euler algorithm in the calculation of x_{n+1} which uses the velocity at t_{n+1} instead of the one at t_n :

$$x_{n+1} = x_n + v_{n+1}\Delta t \quad (\text{II-5a})$$

$$v_{n+1} = v_n + a_n\Delta t \quad (\text{II-5b})$$

This modification in the calculation of x_{n+1} does not affect the algorithm accuracy but makes it more stable, notably for oscillatory systems.¹⁷

Verlet algorithm The Verlet algorithm¹⁸ is a common higher order algorithm. To obtain it, we consider the Taylor expansion for $x_{n-1} = x(t_n - \Delta t)$ like for Eq. (II-3):

$$x_{n-1} = x_n - v_n\Delta t + \frac{1}{2}a_n\Delta t^2 \quad (\text{II-6})$$

By adding and subtracting the expressions for x_{n+1} and x_{n-1} (Eqs. (II-3a) and (II-6), respectively), the Verlet algorithm is obtained:

$$x_{n+1} = 2x_n - x_{n-1} + a_n\Delta t^2 \quad (\text{II-7a})$$

$$v_n = \frac{x_{n+1} - x_{n-1}}{2\Delta t} \quad (\text{II-7b})$$

A particularity of the Verlet algorithm is that the velocity v does not play any role in the integration. The Verlet algorithm is a second-order algorithm, i.e., the global error is of the order of Δt^2 . However, two points which can potentially pose troubles. Firstly, the algorithm is not self-starting as the calculation requires to know the position at time t_{n-1} , which is not known at the beginning. This is generally solved by using another algorithm, such as the Euler algorithm, to calculate the first few steps. The second point is that the velocity is calculated as the difference between two quantities of same magnitude, which can lead to significant rounding error.

Velocity-Verlet algorithm The velocity-Verlet algorithm is a mathematically equivalent version of the Verlet algorithm presented above:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} a_n \Delta t^2 \quad (\text{II-8a})$$

$$v_{n+1} = v_n + \frac{1}{2} (a_n + a_{n+1}) \Delta t \quad (\text{II-8b})$$

The velocity-Verlet algorithm has the advantage to be self-starting and to minimize rounding errors. It is also a popular algorithm when working with conservative systems as it is, like the Verlet algorithm, a symplectic algorithm, i.e., the total energy is conserved for conservative systems. Details of how the velocity-Verlet algorithm is obtained from the Verlet algorithm are given in Appendix A.

Runge-Kutta method The Runge-Kutta method, which was proposed in 1895 by Runge¹⁹ and later developed in 1901 by Kutta,²⁰ is not an algorithm by itself but rather a method which is at the origin of several algorithms. The basic idea of the Runge-Kutta algorithms is to calculate the value of y_{n+1} by dividing the interval $[t_n, t_{n+1}]$ into several subintervals and to evaluate the rate $r = dy/dt$ at each of these intervals. The value of y_{n+1} is then obtained by a weighted average of these rates.

For example, in the case of the fourth-order Runge-Kutta algorithm (RK4), the rate r is evaluated four times, at $t_1 = t_n$, $t_2 = t_n + b_2 \Delta t$, $t_3 = t_n + b_3 \Delta t$ and $t_4 = t_n + b_4 \Delta t$, to obtain the rates r_1 , r_2 , r_3 and r_4 . y_{n+1} is expressed as:

$$y_{n+1} = y_n + (c_1 r_1 + c_2 r_2 + c_3 r_3 + c_4 r_4) \Delta t \quad (\text{II-9})$$

According to the used values of b and c , different Runge-Kutta algorithms can be obtained.

If we apply this fourth order Runge-Kutta algorithm (RK4) to our single moving particle (Eq. (II-2)), we obtain:

$$x_{n+1} = x_n + \frac{1}{6}(k_{1x} + 2k_{2x} + 2k_{3x} + k_{4x}) \quad (\text{II-10a})$$

$$v_{n+1} = v_n + \frac{1}{6}(k_{1v} + 2k_{2v} + 2k_{3v} + k_{4v}) \quad (\text{II-10b})$$

with

$$k_{1x} = a(x_n, v_n, t_n) \Delta t \quad (\text{II-11a})$$

$$k_{1v} = v_n \Delta t \quad (\text{II-11b})$$

$$k_{2x} = a\left(x_n + \frac{k_{1x}}{2}, v_n + \frac{k_{1v}}{2}, t_n + \frac{\Delta t}{2}\right) \quad (\text{II-11c})$$

$$k_{2v} = \left(v_n + \frac{k_{1v}}{2}\right) \Delta t \quad (\text{II-11d})$$

$$k_{3x} = a\left(x_n + \frac{k_{2x}}{2}, v_n + \frac{k_{2v}}{2}, t_n + \frac{\Delta t}{2}\right) \quad (\text{II-11e})$$

$$k_{3v} = \left(v_n + \frac{k_{2v}}{2}\right) \Delta t \quad (\text{II-11f})$$

$$k_{4x} = a(x_n + k_{3x}, v_n + k_{3v}, t_n + \Delta t) \quad (\text{II-11g})$$

$$k_{4v} = (v_n + k_{3v}) \Delta t \quad (\text{II-11h})$$

The Runge-Kutta algorithms are quite popular due to their good accuracy and stability. However, they can be quite computationally expensive and not well adapted to conservative systems as they are not symplectic algorithms.

II.2 Classical Molecular Dynamics simulations

Molecular Dynamics (MD) is a numerical method to compute the dynamics of a system of atoms by individually following the trajectory of each atom. As a good accuracy at the atomic level can be achieved, MD simulations are popular in material sciences to study atomic-scale phenomena such as film deposition, surface etching or atom implantation. Other uses of MD simulations include the study of proteins in biology. However, MD simulations are not well adapted to compute

the dynamics over a large time (μs and longer) or for a (very) large number of atoms. In such cases, kinetic or fluid models are generally more adapted.

In MD simulations, the dynamics of the system is computed by solving, for each atom i , the Newton's equation of motion:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i \quad (\text{II-12})$$

Here, m_i and $\mathbf{r}_i$ are the mass and position of the i -th atom, respectively, and $\mathbf{F}_i$ is the total force exerted on the i -th atom. This force $\mathbf{F}_i$ is computed from the interatomic potential V_i as $\mathbf{F}_i = -\nabla V_i$. This interatomic potential V_i depends on the relative position of the i -th atom with all the other atoms:

$$V_i = V_i(r_{i1}, \dots, r_{ii-1}, r_{ii+1}, \dots, r_{iN}) \quad (\text{II-13})$$

Here, N denotes the number of atoms in the system and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the i -th and j -th atoms located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively.

The interatomic potential function V is a key parameter in MD simulations as the dynamics of the system directly depends on it. Therefore, the used interatomic potential function V needs to accurately describe the interactions between the atoms. Depending on how the potential function V is calculated, two distinct types of MD simulations can be defined.

Ab-Initio MD simulations In Ab Initio MD simulations, the potential V is computed during the simulation from the current disposition of atoms by performing first-principle calculation (DFT). As the potential V is calculated from the current disposition of atoms at each timestep, good accuracy can be achieved. However, such calculations are generally computationally very expensive and, therefore, ab initio MD simulations are not widely used and will be preferred for small systems with a small number of atoms.

Classical MD simulations In classical MD simulations, the potential V is computed before the MD simulation is performed and is provided as input data, either as an analytic expression or as tabulated data. As the potential V does not need to be computed during the simulation, the computational cost is limited. As such, classical MD simulations are widely used and can

accommodate large systems with a large number of atoms. However, the accuracy of classical MD simulations will directly depend on the used potential functions and their ability to accurately describe interatomic interactions.

In this thesis, only classical MD simulations are considered. The used potential functions V are discussed in Sect. II.3.

The system simulated using MD simulations typically represent only a small part of the actual system to limit the calculation time and periodic boundaries can be applied on one or several directions such that atoms crossing one of the boundaries appear on the other side as if the substrate was infinitely large in this direction. For etching simulations as those performed in this thesis, the dynamics of the material surface is studied with empty space above the surface for the injected and etched particles. Therefore, periodic boundaries are only applied on the horizontal (x and y) directions. In the vertical direction (z), fixed boundaries are applied and crossing atoms are considered as etched atoms. To prevent the material from moving due to the incident particle impact, the bottom atoms of the material are fixed.

MD simulations are typically performed under the micro-canonical (NVE) ensemble, such that the number of atoms N , the volume V and the total energy E are constant during the simulation. For this reason, time integration is performed using the velocity-Verlet algorithm (Eq. (II-8)) as it is a symplectic algorithm, i.e., it conserves the total energy over time. The control of the system temperature T is also important. During MD simulations, atoms can be added or removed from the system due to deposition or etching, leading to a modification of the number of atoms and of the material temperature. In real material, the very large number of atoms and the thermal diffusion will compensate for this modification and the temperature will mostly stay uniform across the material. In MD simulations, however, the number of atoms is limited, as mentioned above, and thermal diffusion usually does not take place as the typical simulated timescales (nanoseconds) are much smaller than the typical timescales thermal diffusion takes place (micro-milliseconds). For this reason, artificial thermostating is applied to control the temperature. Different thermostats are available to artificially constrain the system temperature T to a specified target temperature T_0 .

Velocity scaling The simplest way to control the system temperature is to multiply the velocity $\mathbf{v}_i$ of each atom i by a scaling factor λ : $\mathbf{v}_i \rightarrow \lambda \mathbf{v}_i$. The scaling factor λ defines the magnitude of this scaling and is given as the square root of the ratio of the target temperature T_0 to the current temperature T :

$$\lambda = \sqrt{\frac{T_0}{T}} \quad (\text{II-14})$$

This way, the temperature T will converge toward the target temperature T_0 . However, this approach does not allow fluctuations of the temperature.

Berendsen thermostat The Berendsen thermostat²¹ is an improvement of the velocity scaling introduced by Berendsen in 1984. Contrary to the velocity scaling, the Berendsen thermostat allows fluctuations of the temperature. The scaling is done such that the rate of change of the temperature is proportional to the difference between the target and the current temperatures:

$$\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T) \quad (\text{II-15})$$

In this case, the scaling factor λ is given by:

$$\lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T} - 1 \right) \right]^{1/2} \quad (\text{II-16})$$

Here, T is the system temperature, T_0 is the target temperature and Δt is the timestep. The damping parameter τ has a dimension of time and defines how fast the target temperature is reached. A larger damping parameter τ means that it will take longer for the temperature T to reach the target temperature T_0 . It can be noted that when the damping parameter is equal to the timestep (i.e., $\tau = \Delta t$), the Berendsen thermostat is equivalent to the velocity scaling (Eq. (II-14)).

Langevin thermostat The Langevin thermostat²² consists in applying two additional forces to each atom. The total force $\mathbf{F}_T$ applied on an atom is then expressed as:

$$\mathbf{F}_T = \mathbf{F}_C + \mathbf{F}_f + \mathbf{F}_r \quad (\text{II-17a})$$

$$\mathbf{F}_f = -\frac{m}{\tau} \mathbf{v} \quad (\text{II-17b})$$

$$\mathbf{F}_r = \mathbf{A} \sqrt{\frac{k_B T_0 m}{\tau \Delta t}} \quad (\text{II-17c})$$

Here, m is the atom mass, k_B is the Boltzmann constant, T_0 is the target temperature and Δt is the timestep. The damping parameter τ has a dimension of time and defines how fast the target temperature is reached. A larger damping parameter τ means that it will take more time for the temperature T to reach the target temperature T_0 .

The force $\mathbf{F}_C$ in Eq. (II-17a) corresponds to the total force acting on the atom before the application of the two additional forces $\mathbf{F}_f$ and $\mathbf{F}_r$. It originates from the interatomic potential functions and eventual other external forces. The force $\mathbf{F}_f$ corresponds to a frictional drag proportional to the atom velocity $v = |\mathbf{v}|$. This force is always opposing the atom movement and therefore slowing it down. The force $\mathbf{F}_r$ corresponds to the force due to the random bumping of solvent atoms at temperature T_0 into the atom. This magnitude and direction of this force is randomized through the random vector $\mathbf{A}$, different for each atom and at each timestep.

Nosé-Hoover thermostat The Nosé-Hoover thermostat was originally introduced by Nosé²³ and Hoover.²⁴ It provides a way to simulate a system which is, at large times, in the canonical (NVT) ensemble, i.e., the number of atoms N , the volume V and the temperature T are constant.

The idea of the Nosé-Hoover thermostat is to extend the real system by introducing an artificial dynamical variable $\tilde{s}$, associated with a “mass” $Q > 0$ and a velocity $d\tilde{s}/dt > 0$. This artificial variable $\tilde{s}$ plays the role of a time-scaling parameters such that the timescale in the extended system is stretched compared to the real system: $d\tilde{t} = \tilde{s}dt$.

Using the Nosé-Hoover thermostat, the equation of motion is given by:²⁵

$$m \frac{d\mathbf{r}}{dt} = \mathbf{F} - m_i \gamma \frac{d\mathbf{r}}{dt} \quad (\text{II-18a})$$

$$\frac{d\gamma}{dt} = -\frac{1}{\tau_{\text{NH}}^2} \left(\frac{g}{N_{df}} - \frac{T}{T_0} \right) \quad (\text{II-18b})$$

Here, m is the atom mass, $\mathbf{r}$ is the atom position, $\mathbf{F}$ is the total force before the thermostat is applied, T is the system temperature and T_0 is the target temperature. g corresponds to the number of degrees of freedom N_{df} in the real system, possibly increase by 1.²⁵ The strength of the coupling is defined by the effective relaxation time $\tau_{\text{NH}} = (N_{df} k_B T_0)^{-1/2} Q^{1/2}$, with k_B the Boltzmann constant.

II.3 Interatomic potential functions

Interatomic potential functions are a key parameter in MD simulations as they characterize the interactions between the atoms. Numerous different potential functions have been developed to accurately model interatomic interactions, ranging from simple two-body potential functions to complex multi-body potential functions. Different interatomic potential functions for various interactions are available in online repositories such as the NIST's Interatomic Potential Redepository.²⁶ The choice of the used potential functions depends on the simulated system, the atom species and the interatomic interactions to be considered. Here, several interatomic potential functions are presented.

II.3.1 Lennard-Jones potential

The Lennard-Jones (LJ) potential function²⁷ is a two-body potential function introduced in 1924 by Jones. The simplicity of the LJ potential function makes it a popular choice to model van der Waals interactions. It is also used as a simplistic model to approximate covalent or metallic bonds, although it is known that its repulsive part can be too repulsive compared to real materials.

The LJ potential V_{ij} between the i -th and j -th atoms is generally expressed as:

$$V_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (\text{II-19})$$

Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the i -th and j -th atoms located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. σ and ε are the two parameters of the LJ potential function. The parameter σ defines the interaction range, and corresponds to the interatomic distance $r_0 = \sigma$ where the potential is null. The parameter ε defines the interaction strength, and corresponds to the minimum of the potential $V_M = -\varepsilon$ at $r_M = 2^{1/6}\sigma$.

The attractive term of the LJ potential function $((\sigma/r)^6)$ originates from the dispersion forces between atoms which quickly decrease as $r^{1/6}$,^{28,29} whereas the repulsive term $((\sigma/r)^{12})$ accounts for the Pauli repulsive term. The exponent of the repulsive term (12) does not have a strong physical meaning and was chosen for convenience as r^{12} is the square of r^6 , which is computationally advantageous, and because 12 is larger than 6, condition for the potential function to be repulsive for $r_{ij} < 2^{1/6}\sigma$ and attractive for $r_{ij} > 2^{1/6}\sigma$.

The LJ potential function V_{ij} can be normalized to remove all dependency on physical parameters. The normalization is done by setting the normalized distance ξ_{ij} and the normalized potential $\tilde{V}_{ij}$ as:

$$\xi_{ij} = \frac{r_{ij}}{\sigma} \text{ and } \tilde{V}_{ij} = \frac{V_{ij}}{4\varepsilon}$$

The normalized LJ potential function $\tilde{V}_{ij}$ is then expressed as:

$$\tilde{V}_{ij}(\xi_{ij}) = \frac{1}{\xi_{ij}^{12}} - \frac{1}{\xi_{ij}^6} \quad (\text{II-20})$$

The normalized LJ potential function $\tilde{V}_{ij}$ is plotted in Fig. II-1. It presents two characteristic points: the potential is null for $\xi_0 = 1$ and the potential is minimum for $\xi_M = 2^{1/6}$, where $\tilde{V}_M = -1/4$.

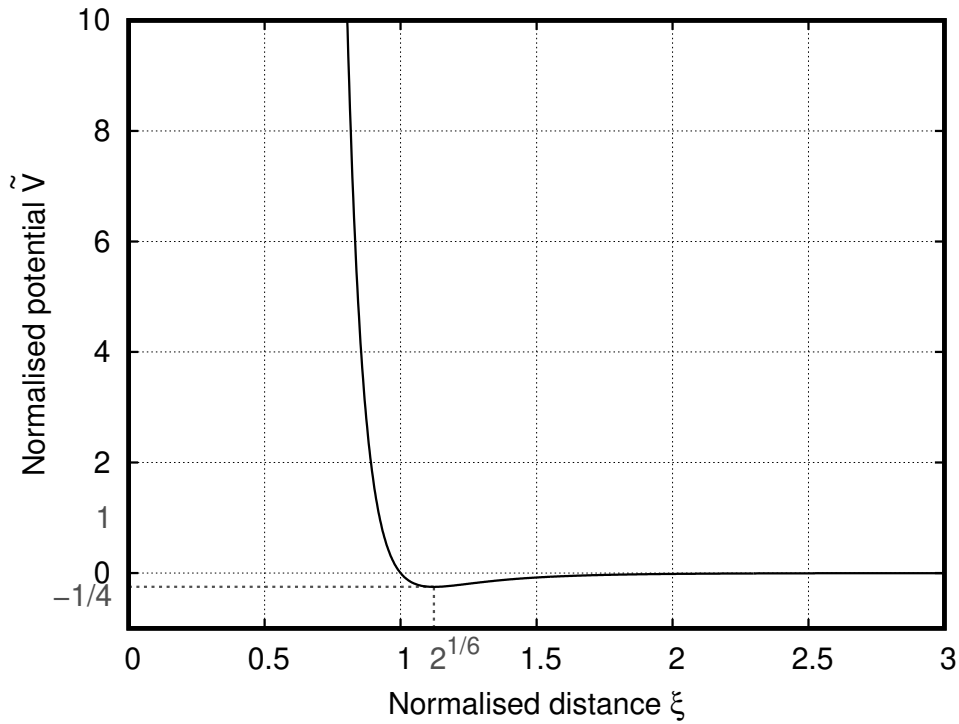


Figure II-1 – Normalized LJ potential function $\tilde{V}_{ij}$. The potential is null for $\xi_0 = 1$ and is minimum for $\xi_M = 2^{1/6}$, where $\tilde{V}_M = -1/4$.

II.3.2 Screen-Coulomb potential

The screen-Coulomb potential function is a purely repulsive two-body potential function in which it is assumed that the atoms are interacting through the Coulomb potential, damped by a screening function. The screening function accounts for the effect of electrons which are suppressing long-range interactions. Screen-Coulomb potential functions are often used to model the interactions at low interatomic distances where other potential functions can lack accuracy.

The screen-Coulomb potential V_{ij} between the i -th and j -th atoms is expressed as:

$$V_{ij}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} \phi\left(\frac{r_{ij}}{a}\right) \quad (\text{II-21a})$$

$$\phi(x) = \sum_k c_k e^{-b_k x} \quad (\text{II-21b})$$

Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the i -th and j -th atoms located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, ε_0 is the vacuum permittivity, Z_i is the atomic number of atom i , e is the elementary charge, a is the screening distance, b_k and c_k are parameters of the screening function $\phi(x)$.

Here, three different screen-Coulomb potential functions are considered: the Ziegler-Biersack-Littmark³⁰ (ZBL), Krypton-Carbon³¹ (Kr-C) and Molière³² potentials. The ZBL potential was obtained as a mean potential of many individual cases calculated by a Hartree-Fock-Slater method (non-relativistic). The Kr-C was obtained as a description of the interaction between krypton (Kr) and carbon (C) atoms, but is a good mean potential for many different interactions between atoms.³³ The Molière potential was obtained from an empirical fitting of the Thomas-Fermi function.

The expression of the screening distance a differs according to the screen-Coulomb potential. For the Ziegler-Biersack-Littmark (ZBL) potential, the screening length a is given by:

$$a = \frac{0.8853a_0}{Z_i^{0.23} + Z_j^{0.23}}, \quad (\text{II-22})$$

whereas the Firsove screening length a_F is used for the Kr-C and Molière potentials:

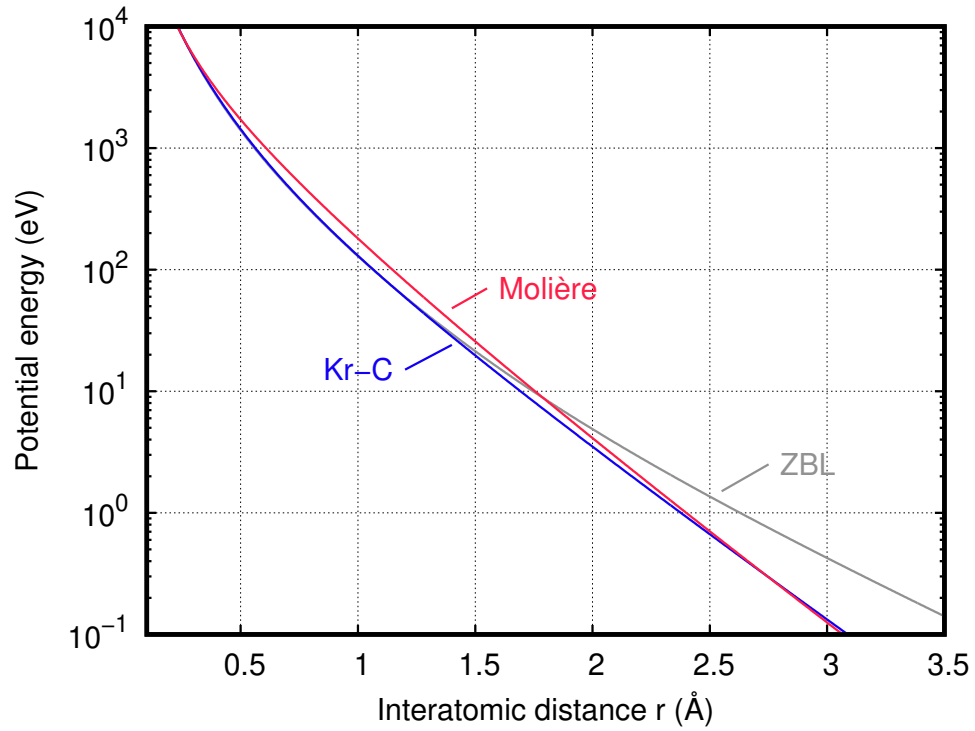
$$a_F = \frac{0.8853a_0}{\left(Z_i^{1/2} + Z_j^{1/2}\right)^{2/3}} \quad (\text{II-23})$$

In both cases, $a_0 = 0.529 \text{ \AA}$ is the Bohr radius.

The values of the parameters b and c of the screening function (Eq. (II-21b)) are given in Table II-1 for the three considered screen-Coulomb potentials. It can be noted that $\sum_k c_k = 1$ for the three potentials. The ZBL, Kr-C and Molière potential functions are plotted in Fig. II-2 for $Z_i = Z_j = 28$, i.e., for Ni-Ni.

Table II-1 – Parameters b and c of the screening function $\phi(x)$ for the ZBL, Kr-C and Molière potential functions.

Parameter	Potential		
	ZBL	Kr-C	Molière
b_1	3.19980	0.278544	0.3
b_2	0.94229	0.637174	1.2
b_3	0.40290	1.919249	6.0
b_4	0.20162	0.0	0.0
c_1	0.18175	0.190945	0.35
c_2	0.50986	0.473674	0.55
c_3	0.28022	0.335381	0.10
c_4	0.02817	0.0	0.0

**Figure II-2** – ZBL, Kr-C and Molière screen-Coulomb potential functions for $Z_i = Z_j = 28$, i.e., for Ni–Ni.

II.3.3 Stillinger-Weber potential

The Stillinger-Weber potential function^{34–36} is a three-body potential. Compared to two-body potential functions, such as the screen-Coulomb potential function described above, the potential also depends on the angle between the atoms.

The total potential energy V_T is assumed to be described as the summation of a two-body part and a three-body part:

$$V_T = \sum_{i < j} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \quad (\text{II-24})$$

Here, $\mathbf{r}_i$ denotes the position of the i -th atom.

We consider here a modified version of the original Stillinger-Weber potential function done by Ohta *et al.*³⁷ for the description of Si–O–F and Si–O–Cl systems.

The two-body part $V_2(\mathbf{r}_i, \mathbf{r}_j)$ is expressed as:

$$V_2(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} \frac{a}{r_{ij}^{2q}} \exp\left(\frac{2d}{r_{ij} - r_C}\right) - \frac{b}{r_{ij}^q} \exp\left(\frac{d}{r_{ij} - r_C}\right) & \text{for } r_{ij} < r_C \\ 0 & \text{for } r_{ij} \geq r_C \end{cases} \quad (\text{II-25})$$

Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the i -th and j -th atoms located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. The parameters a , b , d , q and the cutoff distance r_C depend on the species of the i -th and j -th atoms.

The three-body part $V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ accounts for the angular dependency of the potential function. The potential V_3 between the i -th, j -th and k -th atoms is given as the summation of three functions h :

$$V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h_{jik}(r_{ij}, r_{ik}, \theta_{jik}) + h_{ijk}(r_{ji}, r_{jk}, \theta_{ijk}) + h_{ikj}(r_{ki}, r_{kj}, \theta_{ikj}) \quad (\text{II-26})$$

Here, $\mathbf{r}_i$ is the position of the i -th atom and θ_{jik} denotes the angle between the j -th and k -th atoms at vertex r_i .

The function h_{jik} is given by:

$$h_{jik}(r_{ji}, r_{jk}, \theta_{ijk}) = k_{ijk} |\cos \theta - \Theta_{ijk}|^{\gamma_{ijk}} f_{ij}(r_{ij}) f_{jk}(r_{jk}) \quad (\text{II-27})$$

Here, k_{ijk} , Θ_{ijk} and γ_{ijk} are parameters that depend on the species of the i -th, j -th and k -th atoms. Due to the symmetry of the system, we have $k_{ijk} = k_{kji}$, $\Theta_{ijk} = \Theta_{kji}$ and $\gamma_{ijk} = \gamma_{kji}$. The function $f_{ij}(r_{ij})$ is a step-function-like smooth function such that $f(r) = 1$ when $0 < r \ll r_C$ and $f = 0$ when $r \geq r_C$, with r_C being the cutoff distance. More precisely, $f_{ij}(r_{ij})$ is defined using the two-body term V_2 (Eq. (II-25)) as:

$$f_{ij}(r_{ij}) = \begin{cases} 1 & \text{for } r \leq r_{\min} \\ \frac{V_2(r)}{V_{2\min}} & \text{for } r_{\min} < r < r_C \\ 0 & \text{for } r > r_C \end{cases} \quad (\text{II-28})$$

Here, $r_{\min}$ is the distance where the two-body part $V_2(r)$ is minimum and $V_2(r_{\min}) = V_{2\min}$.

Table II-2 – Parameters of the Stillinger-Weber potential function for several interactions between silicon (Si), oxygen (O) and fluorine (F) obtained from Ref. 38.

Interaction	Two-body V_2				
	a (eVÅ ^{2q})	b (eVÅ ^q)	d (Å)	q	r_c (Å)
Si–Si	170.0	38.3	0.614	1.89	3.6
Si–O	122.0	44.6	0.453	2.52	2.5
Si–F	75.6	41.7	0.269	2.21	2.6
Interaction	Three-body V_3				
	k (eV)	Θ (degree)		γ	
Si–Si–Si	2.14	−0.491		2	
O–Si–O	3.07	−0.509		2	
Si–Si–F	2.08	−0.395		2	

The parameters, obtained from Ref. 38, of the two-body part V_2 for the Si–Si, Si–O and Si–F, and of the three-body part V_3 for Si–Si–Si, O–Si–O and Si–Si–F are given in Table II-2. The two-body part V_2 for Si–Si, Si–O and Si–F are plotted in Fig. II-3a as a function of the interatomic distance r . The three-body part V_3 for Si–Si–Si, O–Si–O and Si–Si–F are plotted in Fig. II-3b as a function of the

angle θ . It is assumed that the interatomic distance with the central atom is at the equilibrium value, i.e., $f_{ij} = 1$.

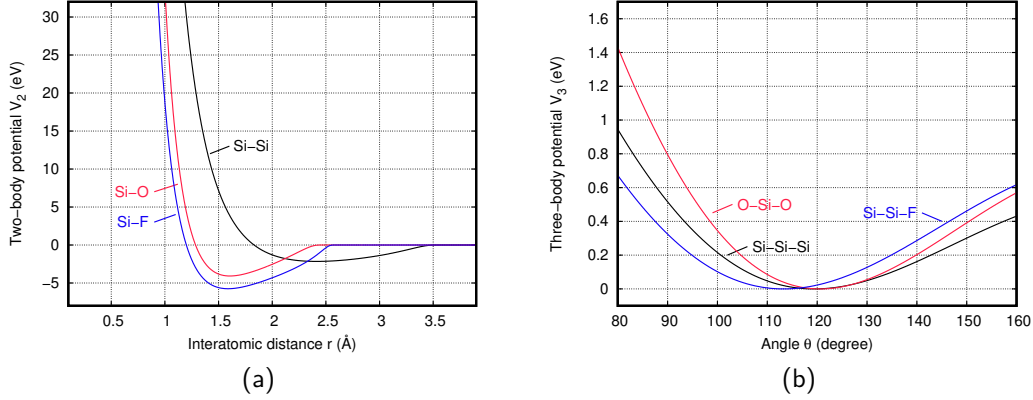


Figure II-3 – Stillinger-Weber potential function. (a) Two-body part V_2 as a function of the interatomic distance r for Si-Si, Si-O and Si-F interactions. (b) Three-body part V_3 as a function of the angle θ for Si-Si-Si, O-Si-O and Si-Si-F interactions. The used parameters are given in Table II-2.

II.3.4 Embedded Atom Method potential

The Embedded Atom Method (EAM) potential function^{39,40} is a multi-body potential function developed in 1984 by Daw and Baskes widely used to model interactions in metallic systems. The EAM potential function is based on the assumption that each atom can be viewed as an impurity embedded in the system made of the other atoms.

The potential V_i for the i -th atom of species α is expressed as the summation of a two-body term and an embedded term which depends on the local electronic density from the surrounding atoms j of species β :

$$V_i(r_{ij}) = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (\text{II-29})$$

Here, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between the i -th and j -th atoms located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. F_α is the embedding energy, that is the energy needed to embed the i -th atom of species α into the electronic cloud formed by

the surrounding atoms, ρ_β is the contribution of the j -th atoms of species β to the electronic cloud at the position of the i -th atom, $\phi_{\alpha\beta}$ is the pairwise potential between the i -th and j -th atoms.

In Eq. (II-29), the density ρ_β only depends on the host species β . Another expression of the EAM potential function was developed in 1984 by Finnis and Sinclair⁴¹ in which the electronic density $\rho_{\alpha\beta}$ depends on the species of both the embedded and host atoms. In this case, the potential V_i for the i -th atom of species α is expressed as:

$$V_i(r_{ij}) = F_\alpha \left(\sum_{j \neq i} \rho_{\alpha\beta}(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (\text{II-30})$$

From the expression of the EAM potential, it can be observed that the multi-body property of the EAM potential function comes from the embedded term $F(\rho)$, and more precisely from the summation over the electronic density ρ .

The three constituting functions $F(\rho)$, $\rho(r)$ and $\phi(r)$ of the EAM potential function are shown in Fig. II-4 for the Ni–Ni interaction of the Fe–Cu–Ni EAM potential function of Ref. 42.

II.4 Material properties

Materials are composed of a collection of interacting atoms. According to the atom species and to how they are arranged, materials present various properties. These material properties include physical properties, i.e., intrinsic properties of the material, such as the density; chemical properties, i.e., properties related to a change of chemical structure, such as combustibility; and mechanical properties, i.e., properties related to the application of constraints on the material, such as the bulk modulus. Understanding the material properties is important to determine the adequate material for a specific use and how several materials can be combined to improve performances.

Interatomic potential functions used in MD simulations are expected to represent the interactions between the atoms. It is therefore important that the inter-

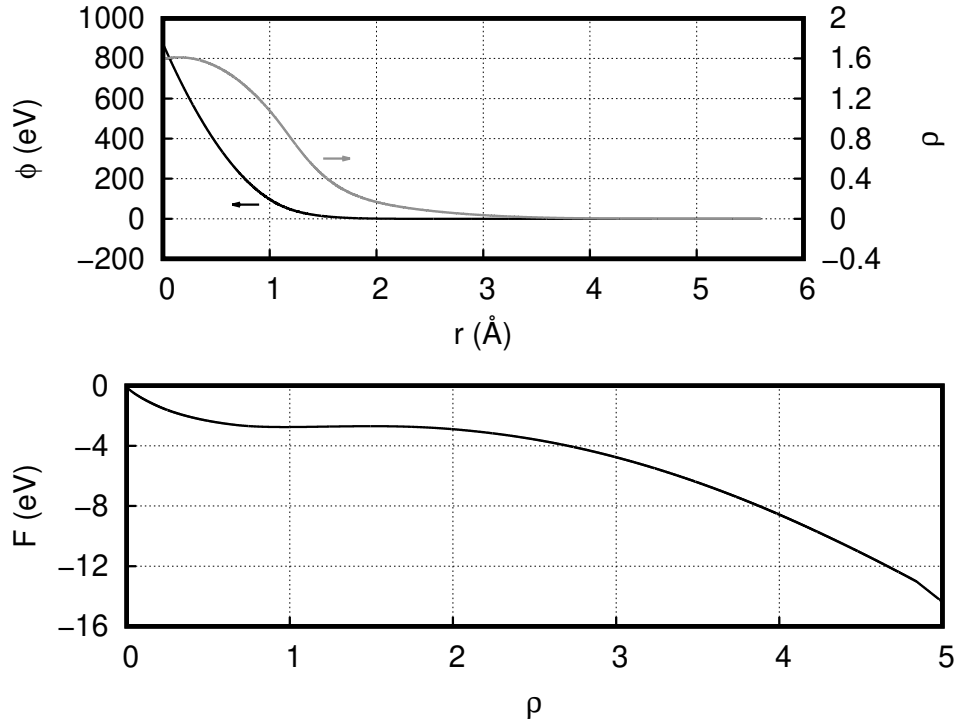


Figure II-4 – The three components of the Ni–Ni EAM potential function from the Fe–Cu–Ni EAM potential of Ref. 42. ϕ , ρ and F are the pair potential, electronic density and embedding energy, respectively.

atomic potential functions are able to accurately reproduce the material properties of the simulated system. Some material properties are discussed in the following.

II.4.1 Lattice constant and cohesive energy

In crystalline materials, atoms are arranged in highly ordered structures where a group of atoms, the basis, is periodically repeated in every direction. The set of the mathematical points where the basis is located is called the lattice. In three-dimensions, the lattice is described by three translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ such that every point $\mathbf{r}'$ of the lattice can be seen as the translation of any point $\mathbf{r}$ of the lattice by a multiple of the translation vectors: $\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$, with u_1 , u_2 and u_3 are arbitrary numbers. The three translation vectors form a parallelepiped of edge length $l_{a1} = |\mathbf{a}_1|$, $l_{a2} = |\mathbf{a}_2|$ and $l_{a3} = |\mathbf{a}_3|$ called the cell. The entire material can be built by the translation of the cell by the translation

vectors $\mathbf{a}_i$, without any empty space or overlapping between the translated cells. It can be noted that, for a single system, the translation vectors $\mathbf{a}_i$ are not unique, there are many nonequivalent possible sets. The cell is therefore also not unique.

A cell is characterized by six lattice parameters, the length of the edges l_{a1} , l_{a2} and l_{a3} , and the angles α , β and γ between the edges. According to the value of these six parameters, the cell is classified among seven crystalline systems.⁴³ The most general crystalline system is the triclinic system where each length and each angle are different, i.e., $l_{a1} \neq l_{a2} \neq l_{a3}$ and $\alpha \neq \beta \neq \gamma$. On the other hand, the cubic crystalline system is the most specific system where the three edges have the same length l_a and the three angles are equal to 90° . These seven crystalline systems are further divided into a total of 14 cells, or lattices. The cubic crystalline system, for example, presents three cells which differ by the number of atoms they contain, the simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) cells. The simple cubic (sc) cell contains a single atom located at a vertex of the cube; the body-centred cubic (bcc) cell contains two atoms, one at a vertex of the cube and one at the centre of the cube; and the face-centred (fcc) cell contains four atoms, one at a vertex of the cube and one at the centre of the three faces sharing this vertex. These three cells are shown in Fig. II-5 along with the diamond cell, which is the typical structure of semiconductor materials such as silicon (Si) or germanium (Ge). Although the diamond cell is not strictly a crystalline cell, it is often considered as one for convenience. The diamond cell is based on the fcc cell with four additional tetrahedrally bonded atoms (Fig. II-5d), and therefore contains eight atoms. As a fraction of the lattice constant l_a , these four additional atoms are located at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, respectively.

The bonding strength of the material depends on the atom species and on their arrangement, i.e., on the crystalline cell. It can be evaluated from the cohesive energy E_C which correspond to the energy required to separate the material constituents into independent neutral atoms at ground state. The cohesive energy E_C is typically given as an energy per atom to have an intensive quantity, i.e., independent of the system size, and is of the order of a few eV.⁴³ By considering the system large enough such that the effect of the boundaries (surfaces) can be neglected, the cohesive energy E_C is estimated as the ratio of the total potential energy E_p to the number of atoms N :

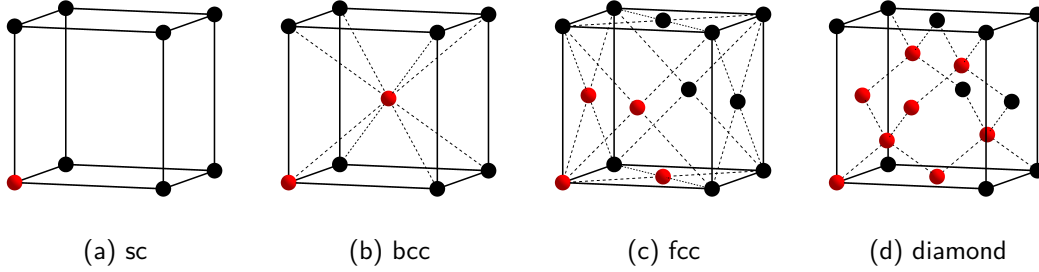


Figure II-5 – Cubic crystalline cells: (a) simple cubic (sc), (b) body-centred cubic (bcc), (c) face-centred cubic (fcc) and (d) diamond. Each cell is a cube of length equal to the length l_a and containing 1, 2, 4 and 8 atoms, respectively. The solid black lines represent the boundaries of the cell, the red spheres represent atoms of the cell and the black spheres represent atoms belonging to adjacent cells. The dash black lines are guides to the eyes.

$$E_C = \frac{E_p}{N}$$

The lattice constant l_a and the cohesive energy E_C both directly depend on the interatomic potential. For a material made of atoms interacting through a LJ potential function and having a fcc structure, it is shown that the lattice constant l_a and the cohesive energy E_C linearly depend on the LJ parameters σ and ε (Eq. (II-31)). Details of the calculations are given in Appendix B.

$$l_a = 1.09\sigma \tag{II-31a}$$

$$E_C = -8.56\varepsilon \tag{II-31b}$$

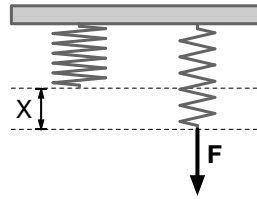
II.4.2 Elastic properties

Under the application of constraints or forces, materials are deformed. How the material is deformed depends on the type of constraints, longitudinal or transverse, and on the material composition, size and geometry. At small constraints, the material is deformed elastically, i.e., deformations are temporary and the material

returns to its initial shape when the constraints are removed. For larger constraints, plastic deformations appear, i.e., permanent deformations which remain after the constraints are removed. When the constraints become very large, the material reaches its rupture point and breaks. The value of the constraints at which plastic deformations appear is known as the yield strength and is a property of each material and typically ranges from 0.1 GPa to 1 GPa. We focus here in the elastic domain, i.e., when the constraints are lower than the yield strength. In this domain, the relation between constraints and deformations is given by the Hooke's law.⁴⁴

The simplest case of elastic deformation is the linear string where the deformation happens in the direction of the applied constraints. In this case, the Hooke's law is expressed as:

$$\mathbf{F} = k\mathbf{X}$$



Here, $\mathbf{F}$ is the longitudinal force exerted on the string (constraint) which has a dimension of force (N), $\mathbf{X}$ is the longitudinal string elongation (deformation) which has a dimension of length (m), and k is the string constant which has a dimension of force per length (N m^{-1}).

For continuous three-dimensional systems, the material can be deformed in a direction different to the direction of the applied constraints. In this case, the Hooke's law is expressed as:

$$\sigma = \mathcal{C}\varepsilon \quad (\text{II-32})$$

Here, σ is the stress tensor which represents the pressure exerted on the material, ε is the strain tensor which represents the relative deformation of the material and $\mathcal{C}$ is the elasticity tensor which is a linear mapping between the strain tensor ε and the stress tensor σ . The stress tensor σ and the elasticity tensor $\mathcal{C}$ have a dimension of pressure (Pa), whereas the strain ε is a dimensionless quantity. The stress tensor σ and strain tensor ε are 3×3 matrices having 9 components ε_{ij} and σ_{ij} , whereas the elasticity tensor is a fourth-order tensor having 81 components

$\mathcal{C}_{ijkl}$. Due to symmetries, ε and σ are symmetric matrices ($\varepsilon_{ij} = \varepsilon_{ji}$ and $\sigma_{ij} = \sigma_{ji}$) and only 6 components are independent. Similarly, $\mathcal{C}$ is a symmetric tensor with 21 independent components.

The notation of the Hooke's law can be simplified by using the Voigt notation. The Voigt notation consists in combining a pair of indices (i, j) into a single index k , i.e., $(i, j) \rightarrow k$, to reduce the order of a symmetric tensor:

$$\begin{array}{ll} 11 \rightarrow 1 & 23 \text{ or } 32 \rightarrow 4 \\ 22 \rightarrow 2 & 13 \text{ or } 31 \rightarrow 5 \\ 33 \rightarrow 3 & 12 \text{ or } 21 \rightarrow 6 \end{array} \quad \begin{pmatrix} M_{11}^1 & M_{12}^6 & M_{13}^5 \\ M_{21} & M_{22}^2 & M_{23}^4 \\ M_{31} & M_{32} & M_{33}^3 \end{pmatrix}$$

Using the Voigt notation, the stress tensor σ and the strain tensor ε are represented by 6×1 matrices and the elasticity tensor $\mathcal{C}$ by a symmetrical 6×6 matrix. The Hooke's law (Eq. (II-32)) is expressed as:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} \mathcal{C}_{11} & \mathcal{C}_{12} & \mathcal{C}_{13} & \mathcal{C}_{14} & \mathcal{C}_{15} & \mathcal{C}_{16} \\ \mathcal{C}_{21} & \mathcal{C}_{22} & \mathcal{C}_{23} & \mathcal{C}_{24} & \mathcal{C}_{25} & \mathcal{C}_{26} \\ \mathcal{C}_{31} & \mathcal{C}_{32} & \mathcal{C}_{33} & \mathcal{C}_{34} & \mathcal{C}_{35} & \mathcal{C}_{36} \\ \mathcal{C}_{41} & \mathcal{C}_{42} & \mathcal{C}_{43} & \mathcal{C}_{44} & \mathcal{C}_{45} & \mathcal{C}_{46} \\ \mathcal{C}_{51} & \mathcal{C}_{52} & \mathcal{C}_{53} & \mathcal{C}_{54} & \mathcal{C}_{55} & \mathcal{C}_{56} \\ \mathcal{C}_{61} & \mathcal{C}_{62} & \mathcal{C}_{63} & \mathcal{C}_{64} & \mathcal{C}_{65} & \mathcal{C}_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} \quad (\text{II-33})$$

In the general case, each of the 21 independent components of the elasticity tensor $\mathcal{C}$ have to be calculated. However, the number of independent components of the elasticity tensor $\mathcal{C}$ can be reduced by considering the symmetries of the system. The number of independent components can be reduced up to 3 in the case of cubic systems, as explained later.

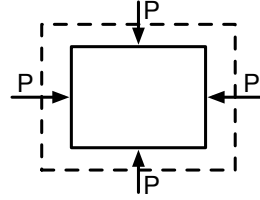
Several mechanical quantities can be defined to characterize the material response to an applied stress.

Bulk modulus The bulk modulus K , or B , is a measurement of the resistance of a material to compression. It has the unit of pascal (Pa) but is generally given in GPa as the bulk modulus is typically very large. It is expressed as the

ratio of the infinitesimal pressure increase to the resulting relative decrease of the material volume or as the ratio of the infinitesimal pressure increase to the resulting relative increase of the material density.

$$K = -V \frac{dP}{dV}$$

$$= \rho \frac{dP}{d\rho}$$

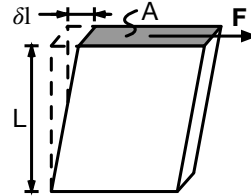


Here, P is the applied pressure, ρ is the material density and V is the initial volume of the material.

Shear modulus The shear modulus G is a measurement of the shear stiffness of a material. The shear modulus has a unit of pascal (Pa) but is typically given in GPa as the shear modulus is generally very large. It is expressed as the ratio of the shear stress to the shear strain.

$$G = \frac{\tau}{\gamma}$$

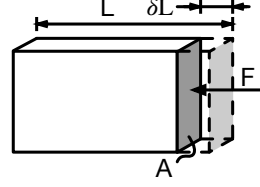
$$= \frac{FL}{A\delta l}$$



Here, τ is the shear stress and γ is the shear strain. F is the magnitude of the applied force on the surface of area A . L is the height of the material and δl is the displacement of the surface of area A in the direction of the applied force $\mathbf{F}$.

Young's modulus The Young's modulus E is a measurement of the strain induced in the direction of the applied stress. The Young's modulus has a unit of pascal (Pa) but is generally given in GPa as it is typically very large. It is expressed as the ratio of the uniaxial stress to the strain.

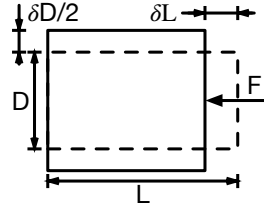
$$Y = \frac{\sigma}{\varepsilon} = \frac{FL}{A\delta L}$$



Here, ε is the uniaxial stress on the material and σ is the strain in the direction of the uniaxial stress ε . F is the magnitude of the applied longitudinal force on the surface of area A . L is the initial size of the material and δl is the change in length of the material.

Poisson's ratio The Poisson's ratio is a measurement of the deformation in the direction orthogonal to the uniaxial applied stress. The Poisson's ratio is a dimensionless quantity. It is expressed as the ratio of the deformation orthogonal to the direction of the applied stress to the deformation along the direction of the applied stress.

$$\nu = -\frac{d\varepsilon_{\text{trans}}}{d\varepsilon_{\text{axial}}} = -\frac{L\delta D}{D\delta L}$$



Here, $\varepsilon_{\text{trans}}$ demotes the deformation in the direction orthogonal to the applied stress and $\varepsilon_{\text{axial}}$ demotes the deformation along the direction of the applied stress. D is the initial size of the material in the transverse direction and δD is the change in size in the transverse direction. L is the initial size of the material in the axial direction and δL is the change in size in the axial direction.

The different mechanical properties are not independent from each other and can be calculated by knowing two others. The relations between the mechanical properties are given in Table II-3.

As mentioned above, the elasticity tensor $\mathcal{C}$ can be simplified by considering the symmetries of the system. The simplest expression of the $\mathcal{C}$ is obtained for a cubic

Table II-3 – Relations between the bulk modulus K , shear modulus G , Young's modulus E and Poisson's ratio ν .

	Modulus			
	K	G	E	ν
(K, G)	—	—	$\frac{9KG}{3K + G}$	$K - \frac{2G}{3}$
(K, E)	—	$\frac{3KE}{9K - E}$	—	$\frac{3K - E}{6K}$
(K, ν)	—	$\frac{3K(1 - 2\nu)}{2(1 + \nu)}$	$3K(1 - 2\nu)$	—
(G, E)	$\frac{EG}{3(3G - E)}$	—	—	$\frac{E}{2G} - 1$
(G, ν)	$\frac{2G(1 + \nu)}{3(1 - 2\nu)}$	—	$2G(1 - \nu)$	—
(E, ν)	$\frac{E}{3(1 - 2\nu)}$	$\frac{E}{2(1 + \nu)}$	—	—

system, where the three axes are identical by symmetry. Therefore, $C_{11} = C_{22} = C_{33}$, $C_{44} = C_{55} = C_{66}$ and $C_{12} = C_{13} = C_{23} = C_{21} = C_{31} = C_{32}$. Also, the off-diagonal shear components and the mixed compression/shear coupling components are zero, i.e., $C_{45} = C_{46} = C_{56} = C_{54} = C_{64} = C_{65} = 0$, $C_{14} = C_{41} = \dots = 0$. The number of independent components of the elasticity tensor $\mathcal{C}$ is reduced to three, namely $\mathcal{C}_{11}$, $\mathcal{C}_{12}$ and $\mathcal{C}_{44}$, and the Hooke's law (Eq. (II-33)) is then expressed as:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} \mathcal{C}_{11} & \mathcal{C}_{12} & \mathcal{C}_{12} & & & \\ \mathcal{C}_{12} & \mathcal{C}_{11} & \mathcal{C}_{12} & & & \\ \mathcal{C}_{12} & \mathcal{C}_{12} & \mathcal{C}_{11} & & & \\ & & & \mathcal{C}_{44} & 0 & 0 \\ & & & 0 & \mathcal{C}_{44} & 0 \\ & & & 0 & 0 & \mathcal{C}_{44} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} \quad (\text{II-34})$$

For a cubic system, the mechanical quantities described above are expressed as:

$$K = \frac{\mathcal{C}_{11} + 2\mathcal{C}_{12}}{3} \quad (\text{II-35a})$$

$$G = \begin{cases} \mathcal{C}_{44} & \text{for shear in (100)} \\ \frac{\mathcal{C}_{11} - \mathcal{C}_{12}}{2} & \text{for shear in (110)} \end{cases} \quad (\text{II-35b})$$

$$\nu = \frac{1}{1 + \frac{\mathcal{C}_{11}}{\mathcal{C}_{12}}} \quad (\text{II-35c})$$



Self-Sputtering of a Lennard-Jones solid

Sputtering^{45,46} is a process of removing atoms from a solid-material surface by the impact of energetic incident ions or atoms. Such an impact causes a collision cascade of atoms inside the material, where billiard-like multiple collisions can eject some atoms from its surface. When the incident ions or atoms are of the same species as those of the atoms constituting the surface material, the sputtering is called the self-sputtering.

Sputtering was first observed in 1853 by Grove¹⁵ in a cathode tube experiment. In 1891, about 40 years later, Crooks⁴⁷ studied some properties of sputtering, which he called “electrical evaporation,” for several different materials. The first realistic mathematical model of sputtering was proposed by Sigmund¹⁶ in 1969, nearly 80 years after the study by Crooks. After the study by Sigmund, many studies, both theoretical and experimental, followed and contributed to a better understanding of the sputtering mechanisms. However, sputtering phenomena are so complex that no mathematical formula to predict an experimentally observable quantity such as the sputtering yield has been derived from the first principles. When first observed in 1853, sputtering was considered as an unwanted effect causing damages on the electrodes and contamination of the plasma. Over time, many applications were found and sputtering became a major tool for surface modifica-

tion, such as surface etching, thin film deposition, and surface cleaning. Especially since the advent of mass production of large-scale-integration (LSI) devices, plasmas have been used for the processing of semiconductor devices.^{6–8} Among various plasma processing, etching processes^{9,11} often employ sputtering techniques combined with surface chemistry, which are called chemical sputtering or reactive ion etching. Plasma processing technologies have contributed significantly to the miniaturization of semiconductor devices as it is the main driving technology for fabricating micro-/nano-scale structures on a semiconductor material surface.^{48–55}

One of the main quantities characterizing sputtering phenomena is the sputtering yield, i.e., the average number of atoms removed from the surface at a single impact of an ion or an atom. For self-sputtering, if the sputtering yield is larger than unity, the surface is etched; if it is less than unity, the material is being deposited. The sputtering yield in general depends on the surface conditions. When a clean surface is exposed to a steady ion beam, the initial sputtering yield can be different from those in later time, when the surface becomes rough and/or the surface chemical compositions change due to the deposition of incident species. In this chapter, unless otherwise stated, we refer to the sputtering yield as that in steady state, where the surface is exposed to the steady incident ions for a sufficiently long time and its surface roughness and chemical compositions no longer change in time.

As one expects, the sputtering yield depends on the incident species and their kinetic energy. Experimentally, the sputtering yield can be measured in ion beam experiments.⁵⁶ Earlier sputtering yield data for single-element materials by single-element ions were extensively compiled in Refs. 57 and 46. More recently, sputtering yields were also measured with mass and energy controlled ion beams experiments for Si- and C-based materials,^{56,58–68} metals,^{69–71} and metal oxides.^{72–78} Sputtering can cause damages on the material surface, which have also been extensively studied.^{79–85}

Sputtering yields can be evaluated theoretically. For example, at relatively high ion incident energy, numerical simulation based on binary-collision models^{30,86,87} can be used to evaluate the sputtering yields of various materials. Under more general conditions, classical molecular dynamics (MD) simulation, where the motions of atoms interacting among themselves are analyzed dynamically with the pre-

determined interatomic potential models, can be used to estimate the sputtering yields.⁸⁸ Unlike binary-collision models, MD simulation can self-consistently model multi-body collisions, which play the dominant role when atoms with relatively low kinetic energies collide with other atoms in a material. MD simulations have been widely used to study sputtering and deposition of Si-based materials^{89–100} and metals.^{101–106}

Although physical phenomena of sputtering are highly complex and the exact sputtering yields may depend sensitively on the nature of atomic interactions of the system, it is also known empirically that the sputtering yield values can be approximately estimated with a relatively small number of physical characteristics of the system, e.g., the incident ion energy, incident ion mass, the atomic mass of the surface material, surface binding energy of the material, etc.¹⁰⁷ This suggests that relatively simple models of atomic interactions account for a large part of the sputtering phenomena involving those atoms.

One of the simplest interatomic potential models is the 12-6 Lennard-Jones (LJ) potential. It has been widely used to study material properties of face-centered cubic (fcc) crystals, transport properties and equation of state¹⁰⁸ for fluids and gases, and the phase transitions among them. The first numerical simulation to examine thermodynamical properties of the system of LJ particles (i.e., particles interacting with the LJ potential) was performed by Wood and Parker.¹⁰⁹ The phase diagram of the LJ system (i.e., the system consisting of LJ particles) is given in Ref. 110.

Although MD simulation has been used to study thermodynamical properties of the system consisting of LJ particles, there seems few studies that determines the sputtering yield of a LJ solid (i.e., a solid consisting of LJ particles) as a function of the incident particle energy. For example, Anders *et al.* studied self sputtering by cluster particles, including single particles, for a clean surface of a fcc crystal consisting of modified LJ particles.¹¹¹ Electronic sputtering (i.e., sputtering by energetic electrons) have been also studied for LJ systems.^{110,112,113} However, it seems no systematic study was performed to determine the steady-state self-sputtering yield of a genuine LJ solid subject to an energetic single particle beam prior to our study presented here. In our study, we use MD simulations to determine the self-sputtering yield of a fcc LJ crystal as a function of the incident particle kinetic

energy and examine how it differs from the experimentally observed sputtering yields of various materials.

The rest of this chapter is structured as follows: Sect. III.1 presents the governing equations solved by MD simulation. Sect. III.2 gives the simulation method. In Sect. III.3, the simulation results, including those by modified LJ potentials, are presented and the comparison with the self-sputtering yields of some metals are discussed. Finally, in Sect. III.4, the conclusion is presented.

III.1 LJ potential function and equations of motion

The LJ potential function V_{LJ} between two particles is commonly expressed as

$$V_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (\text{III-1})$$

where r is the inter-particle distance.

The LJ potential depends on two parameters: the dispersion energy ε , which characterizes the binding energy between the two interacting particles, and the particle radius σ , which corresponds to the inter-particle distance where the potential is null.

Using the following normalized variables

$$\xi = \frac{r}{\sigma} \quad \text{and} \quad \tilde{V} = \frac{V_{\text{LJ}}}{4\varepsilon}, \quad (\text{III-2})$$

the normalized LJ potential function can be written as

$$\tilde{V}(\xi) = \left[\frac{1}{\xi^{12}} - \frac{1}{\xi^6} \right]. \quad (\text{III-3})$$

The normalised potential function presents two characteristic points: the potential $\tilde{V}$ is null for $\xi_0 = 1$ and takes its minimum value $\tilde{V}_{\text{min}} = -1/4$ at $\xi_{\text{min}} = 2^{1/6}$. In the MD simulations performed for this study, the potential function was cut at $\xi_C \simeq 3.7$. The value of normalized potential $\tilde{V}$ at this cut off distance is so small that it has essentially no effect on the dynamics of LJ particles. The normalized potential function $\tilde{V}$ is shown in Fig. III-1.

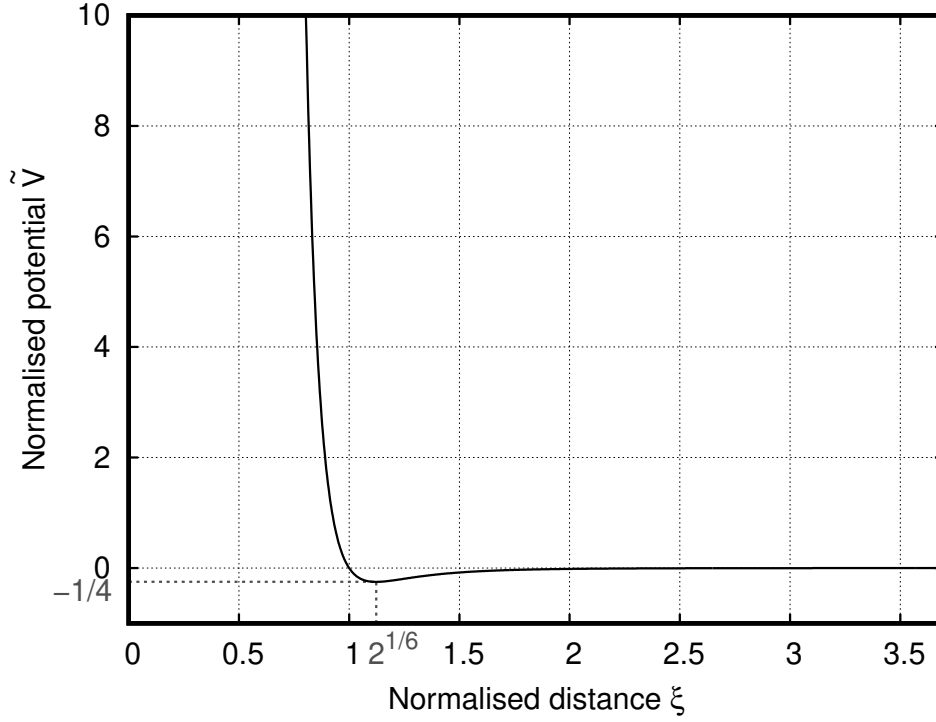


Figure III-1 – Normalized 12-6 LJ potential function $\tilde{V}$ as a function of the normalized distance ξ . The potential takes its minimum $\tilde{V}_{\min} = -1/4$ at $\xi_{\min} = 2^{1/6}$ and is null for $\xi_0 = 1$. In the MD simulations used in this study, the potential function is cut at $\xi_c \simeq 3.7$.

The equations of motion for the LJ system consisting of N particles are give by

$$m \frac{d\mathbf{v}_i}{dt} = -4\epsilon \frac{\partial}{\partial \mathbf{r}_i} \sum_{j(\neq i)} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (\text{III-4})$$

Here $\mathbf{r}_i$ and $\mathbf{v}_i$ denote the position and velocity of the i -th particle ($i = 1, 2, \dots, N$) and the distance between the i -th and j -th particles is represented by $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. $\sum_{j(\neq i)}$ denotes the summation over all particles ($j = 1, 2, \dots, N$) except for the i -th particle. The mass of the LJ particle is denoted by m . To use the LJ system to examine sputtering phenomena, we assume that the LJ particle represents a single atom or ion. In this study, no Coulomb interaction is considered. In actual experiments, incident ions are considered to be charge-neutralized

by an Anger emission process right before their impact on the surface. Base on this premise, we assume that both atom and ion are represented by the same LJ particle and governed by Eq. (III-4) for the sake of simplicity. No Coulomb interaction is considered.

With the normalization similar to Eq. (III-2), i.e.,

$$\boldsymbol{\xi}_i = \frac{\mathbf{r}_i}{\sigma}, \quad \bar{\mathbf{v}}_i = \frac{d\boldsymbol{\xi}_i}{d\tau} = \mathbf{v}_i \frac{T_0}{\sigma} \quad \text{and} \quad \tau = \frac{t}{T_0} \quad \text{with} \quad T_0 = \frac{\sigma}{2} \sqrt{\frac{m}{\varepsilon}},$$

Eq. (III-4) may be normalized as

$$\frac{d\bar{\mathbf{v}}_i}{d\tau} = -\frac{\partial}{\partial \boldsymbol{\xi}_i} \sum_j \tilde{V}(\xi_{ij}), \quad (\text{III-5})$$

where $\xi_{ij} = |\boldsymbol{\xi}_i - \boldsymbol{\xi}_j|$. It should be noted that Eq. (III-5) has no free parameter. Therefore the dynamics of this system is determined only by the initial and boundary conditions. For example, the self-sputtering yield of a LJ solid, which is a dimensionless quantity, depends only on the normalized incident energy and angle of incidence.

The normalized kinetic energy $\mathcal{E}$ of a particle is defined by $\mathcal{E} = \bar{v}^2/2$ with the normalized velocity $\bar{v} = vT_0/\sigma$. Here, $v = |\mathbf{v}|$ and the relation between $\mathcal{E}$ and the dimensional kinetic energy $\mathcal{E} = mv^2/2$ is given by:

$$E = \frac{\mathcal{E}}{4\varepsilon} \quad (\text{III-6})$$

III.2 MD simulation

In this study, classical molecular dynamics (MD) simulations were used to investigate sputtering phenomena of the LJ system. All MD simulations in this work were performed with LAMMPS,¹¹⁴ a classical molecular dynamics simulation code distributed by Sandia National Laboratories, USA, under the GNU General Public License (GPL).

The material used in this study was made of a collection of 27,000 or 122,500 LJ particles (i.e., atoms) arranged in a fcc crystalline structure of lattice constant $l_a \simeq 1.54\sigma$. It had a rectangular shape whose size in the x , y and z directions was

15, 15 and 30 times the lattice constant l_a (27,000 atoms) if the normalized kinetic energy $\mathcal{E}$ of the incident particle satisfied $\mathcal{E} < 1.25 \times 10^3$. If the incident energy was higher, i.e., $\mathcal{E} > 1.25 \times 10^3$, we employed a larger material of 25, 25 and 50 times the lattice constant l_a (122,500 atoms) to ensure that the material subject to the ion bombardment was large enough to incorporate sputtering phenomena with the corresponding large sputtering yields. The material sizes used in this study were selected such that the sputtering yield obtained from MD simulations did not depend on the employed material size. In all cases, the Miller index of the top surface was (100). This crystalline solid is known to be the most stable crystal for LJ particles at low temperature.¹¹⁰ This material was placed at the bottom of a simulation box that had the same horizontal dimensions (i.e., in the x and y directions) and a total height larger than the height of the material by $5l_a$ to keep some space above the initial top surface for particle injections and surface dynamics. In the horizontal directions, periodic boundary conditions were applied, such that the model surface could represent an infinitely large surface. The atoms in a few atomic layers at the bottom of the substrate were fixed in position to prevent the substrate from moving downward by ion impact on the top surface. Atoms leaving the top or bottom surface of the simulation box were considered to be lost and removed from the system. Since the substrate was deep enough, all atoms that left the system did so through the top surface of the simulation box, which means they were either sputtered atoms from the surface or reflected incident atoms or ions.

We also performed MD simulations using larger and deeper materials to confirm that the sputtering yields obtained from MD simulations do not essentially depend on the material size. The material was initially thermalized at a normalized temperature of $\bar{T} = k_B T / 4\varepsilon = 0.006$, with k_B being Boltzmann constant and T being the temperature of the material. This initial temperature corresponds to $T = 300$ K for a typical material with $\varepsilon = 1$ eV.

Sputtering simulations were performed in a manner similar to those of Ref. 106. The flow chart of the simulation cycles is given in Fig. III-2. After setting up a material surface model at $\tau = 0$, a single ion (or atom) was injected into the material surface at a random location of impact on the material surface with a given normalized incident energy $\mathcal{E}$. The incident angle α is defined with respect

to the surface normal (i.e., the z axis). Unless otherwise stated, the normal angle incidence, i.e., $\alpha = 0$, was selected. In our model, atoms and ions were treated equally and no Coulomb interaction was considered, as discussed earlier. The MD

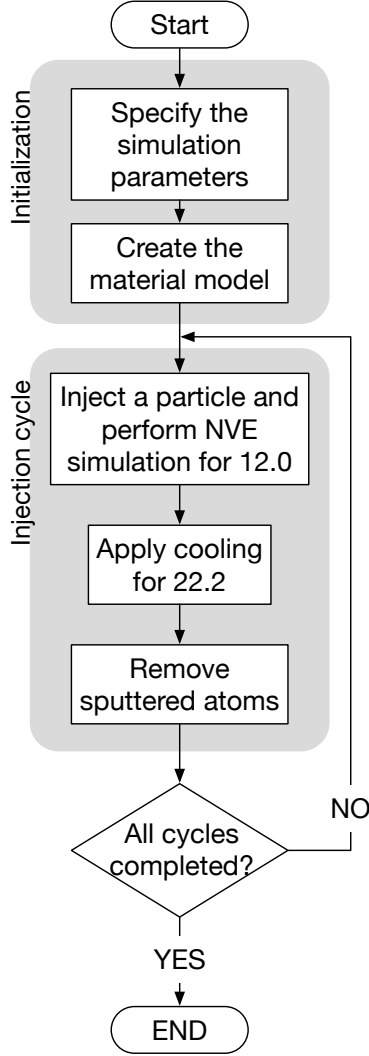


Figure III-2 – Flow chart of the MD simulation. Times are given in units of the normalised time τ .

simulation was performed under the constant total-energy (NVE) conditions up to $\tau = 12.0$. The normalized time step $\delta\tau$ used to integrate the equations of motion was $\delta\tau = 1.7 \times 10^{-3}$ for $\mathcal{E} < 1.25 \times 10^3$ and $\delta\tau = 0.85 \times 10^{-3}$ for $\mathcal{E} > 1.5 \times 10^3$. For a typical material with $\varepsilon = 1$ eV, $\sigma = 1.5$ Å and $m = 58.693$ g mol $^{-1}$ (i.e., the atomic mass of Ni), the selected time steps correspond to 0.1 fs and 0.05 fs, respectively. A Langevin cooling²² was then applied from $\tau = 12.0$ to 30.8 (for the duration of 1.1 ps under the typical material mentioned above), followed by the application of constant temperature (NVT) conditions from $\tau = 30.8$ to 34.2 to emulate a slow-cooling and thermalization process to force the system to reach a thermalized state at $\bar{T} = 0.006$. Such a thermalization process would take place on much longer timescales in real material sputtering. The target temperature $\bar{T}_{\text{target}}$ and damping parameter τ_{damp} (i.e., inverse of the normalized friction coefficient) of the Langevin thermostat used in this study were $\bar{T}_{\text{target}} = 0.006$ and $\tau_{\text{damp}} = 17.1$. At $\tau = 34.2$, all desorbed atoms from the surface (i.e., atoms not bonded with the substrate) were considered as sputtered atoms, removed from the system and a cycle of single ion injection was completed. The Table III-1 gives a summary of the simulation parameters with the corresponding dimensional values.

This cycle was repeated many times until the average number of sputtered

Table III-1 – Summary of the simulation parameters used in this study. Physical quantities are given for $m = 58.8 \text{ g mol}^{-1}$ (i.e., the atomic mass of Ni), $\varepsilon = 1 \text{ eV}$, and $\sigma = 1.5 \text{ \AA}$. Here $\mathcal{E}$ and E denote the normalized and dimensional kinetic energy values of the incident particle.

Parameter			Quantity	
			Normalized	Physical
Timestep $\delta\tau$	if $\mathcal{E} < 1.25 \times 10^3$	($E < 5,000 \text{ eV}$)	1.70×10^{-3}	0.1 fs
	if $\mathcal{E} > 1.25 \times 10^3$	($E > 5,000 \text{ eV}$)	0.85×10^{-3}	0.05 fs
Ion dose	if $\mathcal{E} < 1.25 \times 10^3$	($E < 5,000 \text{ eV}$)	1.87	$8.31 \times 10^{15} \text{ cm}^{-2}$
	if $\mathcal{E} > 1.25 \times 10^3$	($E > 5,000 \text{ eV}$)	0.67	$2.98 \times 10^{15} \text{ cm}^{-2}$
Target temperature $\bar{T}_{\text{target}}$			6.5×10^{-3}	300 K
Langevin thermostat damping parameter τ_{damp}			17.1	1.1 ps
Time for NVE simulation			0.0 to 12.0	0.0 ps to 0.7 ps
Time for Langevin thermostat			12.0 to 30.8	0.7 ps to 1.8 ps
Time for NVT simulation			30.8 to 34.2	1.8 ps to 2.0 ps

atoms per ion injection reached steady state, i.e., became independent of the ion dose. In this study, the cycle was typically repeated 1,000 times (i.e., 1,000 ion injections, which corresponds to a normalized ion dose of 1.87 in the case of 270,000 atoms or 0.67 in the case of 122,500 atoms). Typically the surface roughness due to the ion bombardment also reaches steady state when the sputtering yield no longer depends on the ion dose.

III.3 Self-sputtering simulations

As discussed earlier, the sputtering yield Y is expressed by

$$Y = \frac{N_{\text{Sputtered}}}{N_{\text{Incident}}},$$

where $N_{\text{Sputtered}}$ and N_{Incident} represent the total number of atoms leaving the surface and the total number of injected atoms over a specific time period. If we select a sufficiently short time period to evaluate the sputtering yield, it is called an instantaneous sputtering yield. As discussed earlier, because the surface roughness can change during the sputtering process, the instantaneous sputtering

yield can evolve in time. Typically the surface conditions reach steady state and the instantaneous sputtering yield fluctuates around a constant value after a sufficient ion dose. In what follows, we refer to this constant value in steady state as the sputtering yield.

In the case of self-sputtering, all sputtered atoms and incident ions or atoms are of the same kind and therefore indistinguishable macroscopically. Therefore, all atoms leaving the material surface are counted in $N_{\text{Sputtered}}$, regardless of their origin (from the material or from the incident ions or atoms). (Computationally we could distinguish them, but we do not discuss the difference in this study.) In this case, the threshold between deposition and sputtering is for $Y = 1$, where the number of atoms in the material does not change. For $Y < 1$, incident particles are deposited on the material surface and, for $Y > 1$, the material is being etched.

The initial material model used in this study is shown in Fig. III-3a and the material model after 1,000 particle injections with an normalized incident particle energy $\mathcal{E}$ of 250 is given in Fig. III-3b. It is seen that the surface receded and was roughened due to the sputtering.

III.3.1 Energy and angle dependence of the self-sputtering yield

The dependency of the self-sputtering yield of the LJ system on the normalized incident kinetic energy obtained from MD simulation is given in Fig. III-4. The angle of incidence was normal to the material surface. In this figure, the filled circles represent the sputtering yields obtained from MD simulations of this study and the plus (+) signs are those obtained by Anders *et al.* of Ref. 111. The main difference between this study and Ref. 111 is that Anders *et al.* used a modified LJ potential, connected to the KrC potential³¹ at short separation whereas this study shown in Fig. III-4 is based on the original LJ potential. Furthermore, Anders *et al.* used a clean surface for every particle injection while, in the current work, the material surface is subject to successive particle injections and the self-sputtering yield was evaluated in steady state, where the surface is roughened self-consistently due to the particle injections. However, it seems these differences did not affect the self-sputtering yield much and the results obtained in both studies are in good agreement in the energy range shown here.

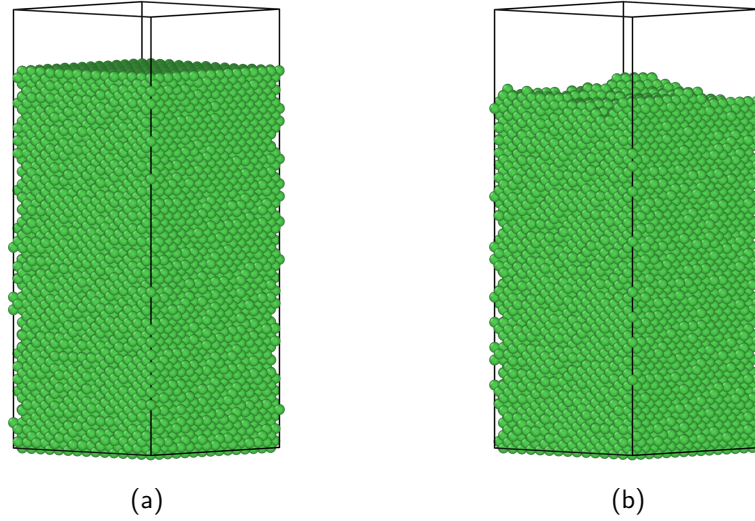


Figure III-3 – Three-dimensional representations of the LJ material model used in this study. Each green sphere represents an LJ particle and the black frame represents the simulation box. The periodic boundary conditions are imposed in the horizontal directions, so that the top surface represents an infinitely wide surface. (a) The initial material model with the (100) top surface, which consists of 27,000 particles. (b) The material model after 1,000 LJ particle injections (i.e., a normalized ion dose of 1.87) with a normalized incident energy of $\mathcal{E} = 250$. Both material models are in thermal equilibrium at a normalized temperature $\bar{T} = 0.006$.

The solid curve is a regression curve obtained from the standard Gaussian Process Regression¹¹⁵ (GPR) based on the 37 data points (filled circles) shown in Fig. III-4. The gray band represents the standard deviation (SD) around the regression curve, representing the uncertainty. The threshold normalized energy, at which $Y = 1$, is $\mathcal{E} \simeq 132$, based on the regression.

It is seen the sputtering yield Y is an increasing function of the normalized incident energy $\mathcal{E}$ increases. However, the way it increases is not monotonic and the gradient of the curve changes around $\mathcal{E} \simeq 200$ and 10^3 . The cause of this structure in the yield curve has not been clarified yet.

The dependency of the self-sputtering yield on the angle of incidence is shown in Fig. III-5 for different normalized incident energies. As seen here, the sputtering yield increases with the increasing angle of incidence α up to its maximum value

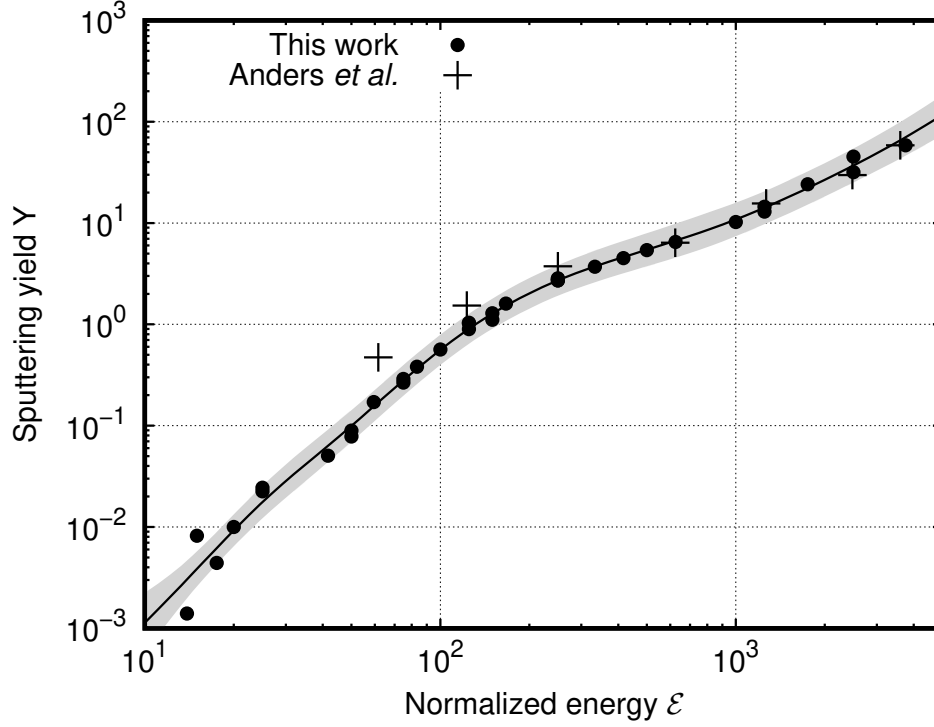


Figure III-4 – Energetic dependency of the self-sputtering yield at normal incidence. The filled circles represent the sputtering yields obtained from MD simulations of this study and the plus (+) signs are those obtained Anders *et al.* of Ref. 111. The solid curve is the prediction obtained using Gaussian Process Regression (GPR) and the gray area corresponds to the uncertainty of the prediction. The predicted sputtering yield curve gives a threshold at $\varepsilon \simeq 132$, at which $Y = 1$.

and then decreases as the angle α further increases. The yield reaches $Y = 1$ at around $\alpha = 80^\circ$. The solid curves in Fig. III-5 are guides to the eye.

III.3.2 Comparison with experiments

Self-sputtering yields of various single-element materials for normal incidence have been obtained experimentally. We now discuss how the experimentally obtained self-sputtering yield values of actual materials are compared with the self-sputtering yields of the LJ system given in Fig. III-4. To make such a comparison, we must identify the values of σ and ε , with which the LJ interatomic function of Eq. (III-1) approximately represents the atomic interactions of actual materials. Especially,

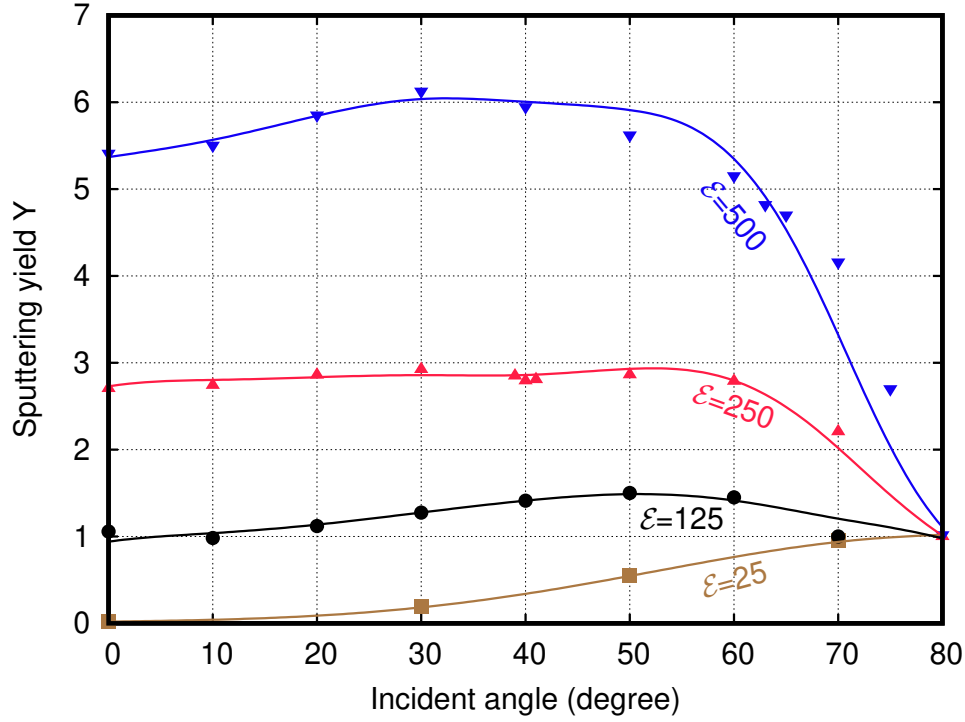


Figure III-5 – Angular dependency of the self-sputtering yield of the LJ solid for four values of $\mathcal{E} = 25, 125, 250$ and 500 . The solid curves are guides to the eye.

as we discussed earlier, the self-sputtering yield of the LJ system for normal incident particles depends only on the normalized ion incident energy $\mathcal{E}$. Therefore, to translate the experimentally obtained sputtering yield Y as a function of the incident ion energy $\mathcal{E}$, we only need to know the corresponding value of ε to convert $\mathcal{E}$ to $\mathcal{E} = E/4\varepsilon$.

A simple way to estimate the corresponding value of ε for an actual material is to use the cohesive energy E_C , i.e., the energy per atom (or per mole) needed to separate the atoms consisting of the material into independent neutral atoms. The cohesive energy has been obtained for most single-element materials.⁴³ On the other hand, our numerical simulation has shown that the cohesive energy per atom of the fcc solid consisting of LJ particles is given by

$$E_C \simeq -8.6\varepsilon. \quad (\text{III-7})$$

at zero temperature and zero pressure. The result is consistent with the earlier

estimate in Ref. 116. By comparing this relation with the cohesive energy of a material obtained either experimentally or by a reliable first-principle calculation, one can estimate the corresponding value of ε . Even for a material that does not form a fcc crystal, one can formally define its corresponding ε value using its cohesive energy E_C and the relation (III-7) as a measure of its cohesiveness.

Similarly one can use the nearest neighbor distance of a material, which has been known for most single-element materials under certain thermodynamical conditions,⁴³ to estimate the corresponding value of σ if the atomic interactions of the material can be approximately represented by the LJ potential. For the fcc solid consisting of LJ particles, our simulation shows that the nearest neighbor distance d , the lattice constant l_a , and σ are related as

$$d \simeq 0.71l_a \simeq 1.1\sigma$$

at zero temperature and zero pressure. The result is consistent with the earlier estimate in Ref. 116. The Table III-2 gives the estimated values of ε and σ for iron (Fe), nickel (Ni), copper (Cu) and gold (Au), based on their cohesive energies and nearest neighbor distances listed in Ref. 43. Note that Ni, Cu, and Au form fcc crystals whereas Fe forms a body-centered cubic (bcc) crystal at standard temperature and pressure.

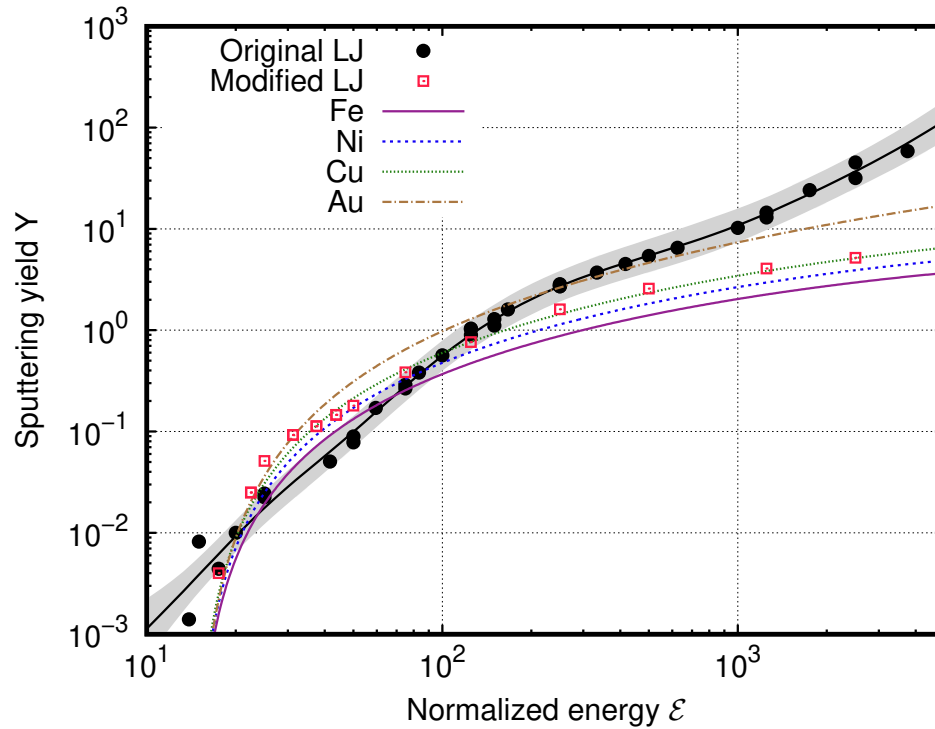
Figure III-6 shows the comparison of the self-sputtering yield of the LJ solid (the same as Fig. III-4) with those of Fe, Ni, Cu, and Au as functions of the normalized energy. The yield curves for Fe, Ni, Cu, and Au are fitting curves to experimental data, given by Yamamura and Tawara,⁵⁷ where the incident ion kinetic energy $\mathcal{E}$ was converted to the normalized energy $\mathcal{E}$ with Eq. (III-6) and ε given in Table III-2. The red squares are the self-sputtering yields obtained for an interatomic potential function that will be discussed in the following subsection.

It is seen in Fig. III-6, the self-sputtering yields for Fe, Ni, Cu, and Au are relatively close to those of the LJ solid when the normalized energy $\mathcal{E} \lesssim 100$, where $Y < 1$ and the deposition takes place. Considering the fact that the vertical axis is a log scale (and therefore magnifies a small difference for small numbers) and the LJ potential is typically considered as a simplistic approximation for the interatomic potentials of Fe, Ni, Cu, and Au atoms, the agreement in this normalized energy

Table III-2 – Evaluated values of ε and σ for Fe, Ni, Cu and Au based on their cohesive energies and nearest neighbor distances listed in Ref. 43.

Parameter	Species			
	Fe	Ni	Cu	Au
ε (eV)	0.50	0.52	0.41	0.45
σ (Å)	2.27	2.28	2.37	2.64

range is rather impressive. However, at higher energies, e.g., $\mathcal{E} \gtrsim 300$, the LJ solid exhibits systematically higher yield values. As discussed earlier, the repulsive part of the LJ potential at short distances is unrealistic, which causes this deviation from the self-sputtering of real materials.¹⁰⁶ In the following subsection, we discuss a possible modification of the LJ potential at short distances.

**Figure III-6** – Comparison between the self-sputtering yield curve of the LJ solid and those of Fe, Ni, Cu, and Au presented by the formula by Yamamura and Tawara.⁵⁷ The red squares are the sputtering yields of the same solid based on the modified LJ potential $\tilde{U}$ of Eq. (III-8).

III.3.3 Potential modification

To lower the self-sputtering yield, we can reduce the collision cross section, allowing the incident particles can penetrate deeper and pass their momenta and energies to a larger number of the substrate atoms, some of which are located in a much deeper region. In this way, fewer recoiled atoms in the material may reach the surface and gain sufficient energy to leave the surface. To do so, we need to reduce the value of the potential function at short distances whereas the attractive part of the potential is unaffected by this modification, so that we can avoid modifying the mechanical and thermodynamic properties of the system as well as the self-sputtering yield at low energies.

The Ziegler-Biersack-Littmark (ZBL) potential³⁰ is widely used to represent a short-range repulsive interaction among atoms. This function is defined for each pair of atomic species and has no adjustable parameter. However, in this study, we use a different function that more or less shifts the repulsive part of the LJ potential toward a smaller particle separation, rather than a generic ZBL potential, which has a totally different functional form from the repulsive part of the LJ potential.

We define a modified normalized LJ potential function $\tilde{U}$ as

$$\tilde{U}(\xi) = g(\xi)\tilde{V}(\xi). \quad (\text{III-8})$$

with

$$g(\xi) = A \tanh [b (\xi - \xi_C)] + 1 - A,$$

where A , B and ξ_C are free parameters. We selected $A = 0.4999$, $\xi_C = 0.8$ and $b = 9.0$ for this study such that the modified potential function would produce the self-sputtering yield curve close to that of a real material, as we shall discuss momentarily. The function $g(\xi)$ serves as an activation function, i.e., $g(\xi) \simeq 1$ for $\xi \geq 1$, $g(\xi_C) \simeq 0.5$, and $0 < g(\xi) \ll 1$ for $0 < \xi \ll 1$, so that $\tilde{U}(\xi) \ll \tilde{V}(\xi)$ at short particle separation whereas $\tilde{U}(\xi) \simeq \tilde{V}(\xi)$ at typical interatomic distances. Fig. III-7b shows the functional form of $g(\xi)$ (on the right vertical axis) as well as $\tilde{U}(\xi)$ and $\tilde{V}(\xi)$ (on the left vertical axis). The functions $\tilde{U}(\xi)$ and $\tilde{V}(\xi)$ are hardly distinguishable below the potential value of 2 or so. Fig. III-7a shows the functional forms of $\tilde{U}(\xi)$ and $\tilde{V}(\xi)$ on a much larger scale. It is seen that the function $\tilde{U}(\xi)$

represents the particle interaction with much smaller particle "radii" when two particles collide at high kinetic energy.

The sputtering yields obtained using this modified potential $\tilde{U}(\xi)$ are shown in Fig. III-6 in red empty squares. It is seen that the self-sputtering yield of the modified LJ system agrees better with those of metals listed in this figure in a wide energy range. The modification above is only to show the effect of reduced interaction radius (and therefore the reduced collision cross section) at high energy impact and we by no means attempt to claim that the functional form of Eq. (III-8) is anything physical. As expected, the self-sputtering yield was significantly reduced and brought to the values close to those of real materials. On the other hand, at a lower energy range of $20 \lesssim \mathcal{E} \lesssim 50$, the self-sputtering yield of the modified LJ system is systematically higher than that of the original LJ system. This is an opposite trend although the radius of impact in this energy range (i.e., the value of ξ that satisfies $\mathcal{E} = \tilde{U}(\xi)$ if $\mathcal{E}$ is in this energy range) is still smaller than that of the original LJ potential $\tilde{V}$. This may be related to the fact that, at shallow collisions, smaller radii of impact allow recoiled energetic particles to escape from the surface region to vacuum by keeping wider openings among atoms located at the lattice sites.

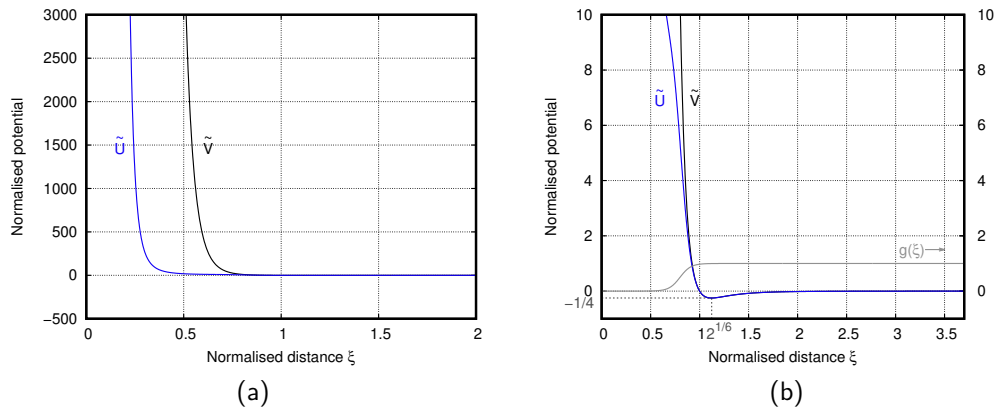


Figure III-7 – Comparison between the normalised LJ potential function $\tilde{V}(\xi)$ and the normalised modified LJ potential function $\tilde{U}(\xi)$ at (a) high energies and (b) low energies. The function $g(\xi)$ used to create $\tilde{U}$ is also plotted.

We now compare the model function $\tilde{U}(\xi)$ with other known model potential

functions at short particle separation. In Fig. III-8, the normalized LJ potential function $\tilde{V}(\xi)$ (denoted as V in the legend) and the normalized modified LJ potential function $\tilde{U}(\xi)$ (denoted as U in the legend) are compared with the normalized ZBL functions for Ni, Cu and Au, as well as the normalized modified EAM potential function for Ni of Ref. 106. In Ref. 106, this interatomic potential function for Ni is denoted as P3 and the MD simulation based on this potential function is shown to provide the self-sputtering yields of Ni in reasonable agreement with the experimental values in the incident ion energy range from 100 eV to 3,000 eV. The ZBL function for Fe overlaps with the ZBL function for Ni in this scale and, therefore, it is not listed here. The normalization was performed with the values given in Table III-2. It is seen that the function $\tilde{U}(\xi)$ is closer to the EAM and ZBL functions listed here than the normalized LJ potential function $\tilde{V}(\xi)$. The sputtering yield is likely to depend on the balance between the repulsive interactions of atoms at close separation and the attractive interactions at intermediate separation. Because the LJ potential is too simplistic to represent the attractive interactions for real atoms, we do not attempt to construct a repulsive interaction model for a better agreement between the simulation and experimental results within the framework of the LJ system of this study.

III.4 Conclusions

MD simulations were performed to obtain the universal curve of the self-sputtering yield for the (100) surface of the LJ fcc crystal at low surface temperature as a function of the normalized incident particle kinetic energy for normal incidence. We have also obtained the self-sputtering yields of the fcc LJ crystal as functions of the angle of incidence at some selected normalized incident energies. Because the most stable crystalline structure of such a system is the fcc crystal and its self-sputtering yield depends only on the normalized incident energy and the angle of incidence, the sputtering yield curves presented here serve as the fundamental reference data for the LJ potential. We also compared the self-sputtering yield of the LJ solid with those of Fe, Ni, Cu, and Au as functions of the incident ion energy for normal incidence. It should be noted that Ni, Cu, and Au form fcc

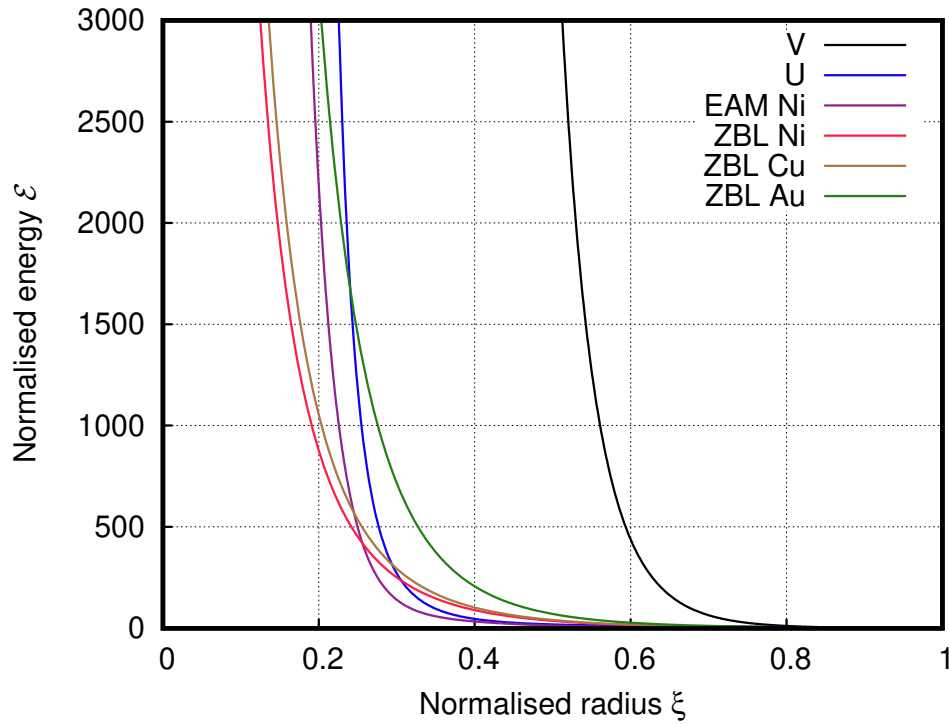


Figure III-8 – Comparison among different potential functions at short separation. The black and blue curves represent the normalized LJ potential function $\tilde{V}(\xi)$ (denoted as V in the legend) and the normalized modified LJ potential function $\tilde{U}(\xi)$ (denoted as U in the legend). The purple curve is the normalized modified EAM potential function for Ni used in Ref. 106. The red, gold, and green curves are the normalized ZBL functions for Ni, Cu, and Au, respectively. The ZBL function for Fe overlaps with the ZBL function for Ni in this scale. The normalization was performed with the values given in Table III-2.

crystals whereas Fe forms a bcc crystal at standard temperature and pressure. Nevertheless, the agreement is reasonable at low ion incident energy where deposition typically takes place. At higher incident energy, however, the self-sputtering yield of the LJ solid differs significantly from those of the actual materials. This is because, as pointed out by various previous studies, the repulsive interactions of the LJ potential do not represent those of actual atoms at short distances.

If the incident particle is a different species from those of the surface material, the sputtering yield depends on more parameters characterizing the difference in species, in addition to the ion incident energy, even if all particles interact with the

LJ potentials. The extension of the current study to such a system may serve as a reference for more general sputtering phenomena of real materials and is discussed in the next chapter.

Why are physical sputtering yields similar for incident ions with different masses? — physical sputtering yields of the LJ system

Plasma etching has significantly contributed to the miniaturization of semiconductor devices as it is one of the main driving technologies for the fabrication of micro/nano-scale structures on wafer surfaces.^{6–10} Plasma etching refers to the process of removing atoms from a surface by the impact of energetic and/or chemically reactive incident species (ions and radicals, typically) generated in a plasma. Chemically reactive species adsorbed on the surface modify the surface chemical compositions and the impact of energetic incident ions causes collision cascades of atoms inside the material, whose billiard-like multiple collisions can lead to the ejection of some atom from the surface. Synergetic effects between the chemical modification of the surface and the ion impact determine the sputtering yield (i.e., the average number of atoms removed atoms per ion impact) and, therefore, such etching is called reactive ion etching (RIE).^{11–13} If no modification of the surface chemical composition takes place, the process is called physical sputtering or physical etching.^{45,46}

When deep and narrow structures such as high-aspect-ratio holes and slits used, for example, in three-dimensional (3D) NAND flash memory devices⁴ are formed with RIE processes, ion incident energies are typically set high. It is known that, even in RIE processes, the higher the ion incident energy becomes, the more physical the nature of etching becomes. For example, with high ion incident energies, the sputtered (or desorbed) species from the surface are typically single atoms or fractions of molecules with small numbers of atoms rather than large molecules.⁹⁹ Such sputtered species typically have high sticking probabilities with material surfaces, resulting in the redeposition of sputtered materials on the sidewalls of deep structures.^{117–119} Sputtering deposition processes are another example where physical sputtering plays an important role in modern industry. Sputtered species from the target surface are used to form thin films over micro/nano-scale structures on a wafer facing the target surface. For example, in the case of ionized magnetron sputtering, the deposited thin film on the wafer is subject to simultaneous etching and deposition processes, depending on the fluxes and energies of incident ion and neutral species.^{54,120–122}

Thus physical sputtering plays important roles in various industrial applications even when some surface chemical reactions take place during the etching processes. Experimentally, sputtering yields can be evaluated by beam experiments.⁵⁶ For example, sputtering yield data for single-element materials by single-element ion impact obtained before the mid-90s are compiled in Ref. 57. The sputtering yields of various materials, including composite materials, by various ionic species were also obtained in more recent experiments for metals,^{69–71,123–125} metal-oxides,^{72–78} and Si- and C-based materials^{56,61–68,126,127} Sputtering can cause damages on the etched material surface, which have also been extensively studied.^{79–85,128}

Sputtering yield can also be evaluated theoretically. For example, the sputtering yields can be evaluated with numerical simulations based on binary-collision models^{30,86,87} at relatively high ion incident energies. Under more general conditions, classical molecular dynamics (MD) simulations, where the motion of atoms interacting among themselves are analysed with predetermined interatomic potential models, can be used to evaluate the sputtering yields.⁸⁸ Unlike binary-collision models, MD simulations can self-consistently model multi-body collisions, which

play the dominant role when atoms with relatively low kinetic energies collide with other atoms in materials. MD simulations have been widely used to study sputtering and deposition processes of metals^{101–106} as well as Si- and C based materials.^{89–100,129}

The experimental and simulation data obtained so far indicate that, for a given surface material and ion incident energy, the sputtering yields tend to depend weakly on the mass of incident ion species, except for extremely small ions such as helium (He), if the sputtering is dominated by physical sputtering. For example, Fig. IV-1 shows the comparison of the experimentally obtained sputtering yields of silicon (Si), iron (Fe), nickel (Ni) and copper (Cu) for self-sputtering and sputtering by noble gas ions, i.e., helium (He^+), neon (Ne^+), argon (Ar^+), krypton (Kr^+) and xenon (Xe^+). Silicon (Si) and iron (Fe) have diamond and body-centered cubic (bcc) crystalline structures whereas nickel (Ni) and copper (Cu) have face-centered cubic (fcc) crystalline structures. The data are taken from Ref. 57 and the solid curves are the empirical fitting curves proposed by Yamamura and Tawara.⁵⁷ It is seen that, except for He^+ sputtering, the sputtering yield hardly depends on the incident species in an energy range from about 100 to several keV. At larger incident energies, a dependence on the incident species is observed. On the other hand, the sputtering yields by He^+ ions are lower in most of the energy range. Similar weak mass dependence is also observed for the sputtering yields of composite materials.^{74,75}

The weak dependence of sputtering yields on the incident ion mass in a relatively low ion incident energy range seems a generic property of sputtering. The goal of this study is to understand why it is so and clarify how the sputtering yield depends on the system parameters such as the atomic masses and incident ion energy. To achieve this goal, we examine sputtering phenomena using molecular dynamics simulations of atoms interacting with simple interatomic potential functions. The reason we use simple interatomic potential functions, rather than realistic ones, is that we conjecture that this generic property does not depend on the details of specific atomic interactions of the system we consider.

One of the simplest and most widely used interatomic potential functions to describe material and fluids is the Lennard-Jones (LJ) potential. The simplicity of the LJ potential function makes it a popular choice to model approximate covalent

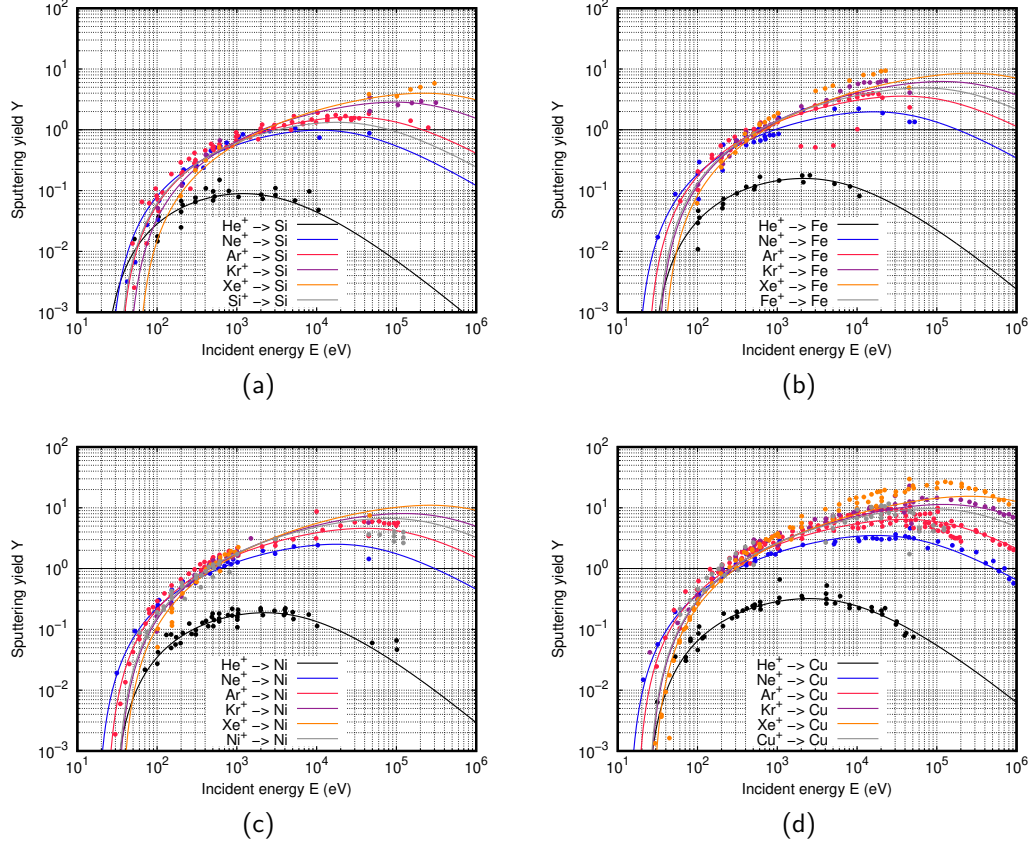


Figure IV-1 – Experimentally obtained self-sputtering and sputtering yields of (a) Si, (b) Fe, (c) Ni, and (d) Cu by He^+ , Ne^+ , Ar^+ , Kr^+ and Xe^+ ions as functions of the incident ion energy. The data are from Ref. 57 and the solid curves are the empirical fitting functions given in the same reference.

and metallic bonds as well as van der Waals interactions. The LJ potential has been widely used for the study of thermodynamics properties,¹⁰⁹ transport properties, and equations of state¹⁰⁸ for solids, fluids, and gases, and the phase transitions among them.^{110,130–133}

A recent study¹³⁴ has shown that the Lennard-Jones (LJ) system, i.e., the system of particles interacting with the LJ potential functions, can reproduce the sputtering yields of real materials reasonably well except for a high ion-incident-energy range, where the discrepancy between the repulsive potential of the LJ system and those of real atoms becomes significant.^{111,134} Therefore, in this study,

we extend the LJ-system of Ref. 134 to that for general sputtering, i.e., the system where the surface material and incident particles are of different species, and compare the sputtering yields of the model system with those of real materials in a relatively low ion incident energy range. To keep the system as simple as possible, we construct a single-element solid consisting of LJ particles (i.e., particles interacting with the LJ potential) and inject energetic particles having an LJ-like repulsive potential and a different mass to the solid surface. The system is intended to emulate a solid interacting with noble gas ions such as Ar^+ . As we shall discuss in the following section as well as in Append. C.1, in this way, we can minimise the number of system parameters while keeping the essential physical mechanisms that govern the sputtering phenomena. Such a system may be considered as a minimal extension of the LJ system of a single element used in Chap. III (Ref. 134). Because the LJ system is one of the most extensively studied models for materials and fluids, determining its sputtering properties may also be considered valuable in itself. Therefore, in this study, we shall examine sputtering properties of the LJ system of a single element by repulsive particles of a different species.

The rest of this chapter is structured as follow: Sect. IV.1 presents the LJ potential functions used in this study. Sect. IV.2 outlines the simulation method. In Sect. IV.3, the sputtering yields of the LJ system obtained from MD simulations are presented and compared with the corresponding experimental values. The conclusions are presented in Sect. IV.4.

IV.1 LJ Potentials and equations of motion

In this study, the interactions among atoms are represented by the Lennard-Jones (LJ) potential function.²⁷ No Coulomb interaction was taken into account in this study because, in real systems, incident ions are expected to be charge-neutralized by an Auger emission process right before they impact the surface.¹³⁵ The LJ potential function depends on two parameters: the “length” parameter σ , which is the interatomic distance at which the LJ potential is null, and the “binding” parameter ε , which represents the strength of the interaction. The simplicity of

the LJ potential function makes it a popular choice to model approximate covalent or metallic bond interactions. It is, however, known that the short-range part of the LJ potential is too repulsive compared with the interatomic potential of real atoms.^{111,134}

In this study, we consider two atomic species. The interaction among atoms that constitute the surface material is modelled with a full LJ potential function $V_{\alpha\alpha}(r)$. The interaction between an atom of the surface material and an injected atom is modelled with a repulsive potential function $V_{\alpha\beta}(r)$. The interaction among injected atoms is modelled with another repulsive potential function $V_{\beta\beta}(r)$. The expressions of these functions are given by

$$V_{\alpha\alpha}(r) = 4\varepsilon_{\alpha\alpha} \left[\left(\frac{\sigma_{\alpha\alpha}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\alpha}}{r} \right)^6 \right] \quad (\text{IV-1a})$$

$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} \quad (\text{IV-1b})$$

$$V_{\beta\beta}(r) = 4\varepsilon_{\beta\beta} \left(\frac{\sigma_{\beta\beta}}{r} \right)^{12} \quad (\text{IV-1c})$$

Here r denotes the interatomic distance. The subscript α or β indicate that the atom species.

It should be noted that the parameters $\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12}$ and $\varepsilon_{\beta\beta}\sigma_{\beta\beta}^{12}$ always appear as these combinations and, for example, $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are not individually defined in the framework of this study. However, we keep these parameters as they are because, as we shall discuss later, the corresponding values of $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ can be defined separately for most atoms, including noble gases, and can be used for the comparison between the simulation results and experimental observations. Weakly bound atoms such as noble gas atoms tend to have small ε values while σ values are similar to those of other atoms. If the interactions among all atoms are represented by full LJ potential functions, the potential energy system of Eq. (IV-1) is valid in the limit of $\varepsilon_{\alpha\beta}/\varepsilon_{\alpha\alpha} \rightarrow 0$ and $\varepsilon_{\beta\beta}/\varepsilon_{\alpha\alpha} \rightarrow 0$. (See Appendix C.1)

The dynamics of a LJ system of N atoms of different species is governed by following two equations of motion:

$$\begin{aligned}
m_\alpha \frac{d\mathbf{v}_i}{dt} &= -4\varepsilon_{\alpha\alpha} \sum_{j \in \alpha} \frac{\partial}{\partial \mathbf{r}_i} \left[\left(\frac{\sigma_{\alpha\alpha}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\alpha\alpha}}{r_{ij}} \right)^6 \right] - 4\varepsilon_{\alpha\beta} \sum_{j \in \beta} \frac{\partial}{\partial \mathbf{r}_i} \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} \quad (i \in \alpha) \\
m_\beta \frac{d\mathbf{v}_i}{dt} &= -4\varepsilon_{\alpha\beta} \sum_{j \in \alpha} \frac{\partial}{\partial \mathbf{r}_i} \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - 4\varepsilon_{\beta\beta} \sum_{j \in \beta} \frac{\partial}{\partial \mathbf{r}_i} \left(\frac{\sigma_{\beta\beta}}{r_{ij}} \right)^{12} \quad (i \in \beta)
\end{aligned}$$

It is understood that the summation over j is taken in such a way that $j \neq i$. Here m_α and m_β are the atomic masses of species α and β , $\mathbf{v}_i$ is the velocity of the i -th atom, $\mathbf{r}_i$ is the position of the i -th atom, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the interatomic distance between the i -th and j -th atoms. $i \in \alpha$ means that the i -th atom is of species α . $\sum_{j \in \alpha}$ and $\sum_{j \in \beta}$ denote the summation over all atoms $j \neq i$ belonging to species α only and β only.

By setting the following normalised variables

$$\boldsymbol{\xi}_i = \frac{\mathbf{r}_i}{\sigma_{\alpha\alpha}}, \quad \bar{\mathbf{v}}_i = \frac{d\boldsymbol{\xi}_i}{d\tau} = \mathbf{v}_i \frac{T_0}{\sigma_{\alpha\alpha}} \quad \text{and} \quad \tau = \frac{t}{T_0} \quad \text{with} \quad T_0 = \frac{\sigma_{\alpha\alpha}}{2} \sqrt{\frac{m_\alpha}{\varepsilon_{\alpha\alpha}}}, \quad (\text{IV-2})$$

and system parameters

$$\mu = \frac{m_\beta}{m_\alpha}, \quad \rho = \frac{\sigma_{\alpha\beta}}{\sigma_{\alpha\alpha}} \left(\frac{\varepsilon_{\alpha\beta}}{\varepsilon_{\alpha\alpha}} \right)^{\frac{1}{12}} \quad \text{and} \quad \rho_2 = \frac{\sigma_{\beta\beta}}{\sigma_{\alpha\alpha}} \left(\frac{\varepsilon_{\beta\beta}}{\varepsilon_{\alpha\alpha}} \right)^{\frac{1}{12}}$$

The normalized equations of motion can then be written as:

$$\frac{d\bar{\mathbf{v}}_i}{d\tau} = - \sum_{j \in \alpha} \frac{\partial}{\partial \boldsymbol{\xi}_i} \left(\frac{1}{\xi_{ij}^{12}} - \frac{1}{\xi_{ij}^6} \right) - \sum_{j \in \beta} \frac{\partial}{\partial \boldsymbol{\xi}_i} \left(\frac{\rho}{\xi_{ij}} \right)^{12} \quad (i \in \alpha) \quad (\text{IV-3a})$$

$$\mu \frac{d\bar{\mathbf{v}}_i}{d\tau} = - \sum_{j \in \alpha} \frac{\partial}{\partial \boldsymbol{\xi}_i} \left(\frac{\rho}{\xi_{ij}} \right)^{12} - \sum_{j \in \beta} \frac{\partial}{\partial \boldsymbol{\xi}_i} \left(\frac{\rho_2}{\xi_{ij}} \right)^{12} \quad (i \in \beta) \quad (\text{IV-3b})$$

Because incident species have only repulsive interaction with other atoms, they are most likely to leave the surface together with the surface atoms when sputtering takes place. Therefore, we expect incident species hardly interact among themselves and the second term of the LHS of Eq. (IV-3b) hardly affects the sputtering yield. Therefore, for the sake of simplicity, we assume in this study

$$\rho = \rho_2.$$

With these assumptions, the system now depends only on two parameters μ and ρ and the equations of motion (Eq. (IV-3)) can be written as:

$$\frac{d\bar{\mathbf{v}}_i}{d\tau} = -\frac{\partial}{\partial \bar{\boldsymbol{\xi}}_i} \left[\sum_{j \in \alpha} \tilde{V}_{\alpha\alpha}(\xi_{ij}) - \sum_{j \in \beta} \tilde{V}_{\alpha\beta}(\xi_{ij}; \rho) \right] \quad (i \in \alpha) \quad (\text{IV-4a})$$

$$\mu \frac{d\bar{\mathbf{v}}_i}{d\tau} = -\frac{\partial}{\partial \bar{\boldsymbol{\xi}}_i} \sum_j \tilde{V}_{\alpha\beta}(\xi_{ij}; \rho) \quad (i \in \beta) \quad (\text{IV-4b})$$

with the normalized interatomic functions defined by

$$\begin{aligned} \tilde{V}_{\alpha\alpha}(\xi) &= \left[\frac{1}{\xi^{12}} - \frac{1}{\xi^6} \right] \\ \tilde{V}_{\alpha\beta}(\xi; \rho) &= \left(\frac{\rho}{\xi} \right)^{\frac{1}{12}} \end{aligned}$$

Now we examine the interatomic potential functions of this system. The function $\tilde{V}_{\alpha\alpha}$ takes its minimum value at $\xi = \xi_M = 2^{1/6}$, i.e., $\tilde{V}_{\alpha\alpha}(\xi_M) = -1/4$ and becomes null at $\xi = 1$. The repulsive potential function $\tilde{V}_{\alpha\beta}$ becomes unity at $\xi = \rho$, which indicates that the parameter ρ represents a typical interaction range between a surface atom α and an incident atom β relative to the interaction range between two surface atoms. Therefore, in this article, we call ρ the relative interaction range of the incident ion. Figure IV-2 shows the normalised LJ potential $\tilde{V}_{\alpha\alpha}$ and three different repulsive potential $\tilde{V}_{\alpha\beta}$ with three different values of $\rho = 1.0, 0.5$ and 2.0 .

With the normalization of Eq. (IV-2), any energy quantity is normalised with $4\varepsilon_{\alpha\alpha}$, as we have seen $\tilde{V}_{\alpha\alpha} = V_{\alpha\alpha}/4\varepsilon_{\alpha\alpha}$. The normalized kinetic energy of an atom is also defined as

$$\mathcal{E} = \frac{1}{2} \bar{v}^2 = \frac{E}{4\varepsilon_{\alpha\alpha}},$$

where $E = mv^2/2$ is the kinetic energy in dimensional units, with v being the magnitude of the incident particle velocity $v = |\mathbf{v}|$ and $\bar{v} = vT_0/\sigma_{\alpha\alpha}$.

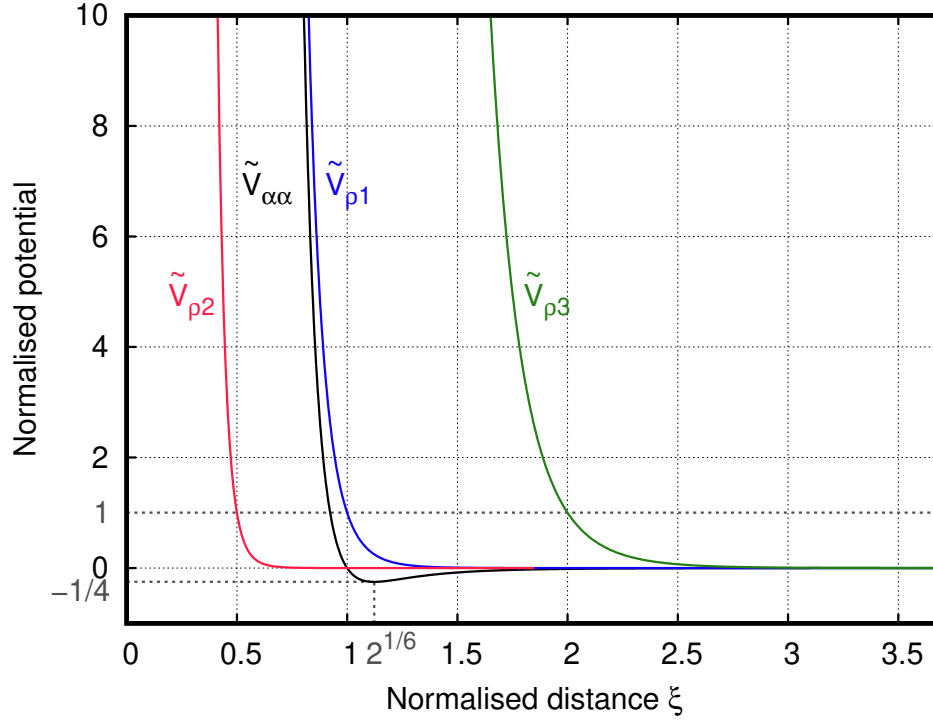


Figure IV-2 – Normalized LJ potential $\tilde{V}_{\alpha\alpha}$ and normalized repulsive potential $\tilde{V}_{\alpha\beta}$ for three different values of $\rho = 1.0, 0.5$ and 2.0 , denoted by $\tilde{V}_{\rho_1}$, $\tilde{V}_{\rho_2}$ and $\tilde{V}_{\rho_3}$, respectively.

IV.2 Outline of MD simulations

MD simulation was performed to examine the sputtering phenomena of the LJ system. All MD simulations in this study were performed with the classical MD simulations code LAMMPS^{114,136} distributed under the GNU General Public License (GPL) license by Sandia National Laboratories, USA.

The material used in this study is made of 27,000 atoms arranged in a face-centered cubic (fcc) crystalline structure of lattice constant $l_a = 1.54\sigma$. (Here and in what follows, the subscript $\alpha\alpha$ of Eq. (IV-1a) is omitted for conciseness unless needed.) It had a rectangular shape with a dimension of 15, 15 and 30 times the lattice constant l_a in the x , y and z directions, respectively. In all cases, the Miller index of the top surface was (100). The material was placed at the bottom of a simulation box having the same size in the horizontal directions, i.e.,

x and y directions, while having a size of 35 times the lattice constant l_a in the z direction to maintain some space above the material for particle injection and surface dynamics. Periodic boundary conditions were applied in the horizontal directions to model an infinitely large surface. The position of the atoms in a few layers at the bottom of the material were fixed to prevent the material from moving downward due to the particle injection. All atoms leaving the simulation box were considered lost and removed from the system. Since the material is thick enough, all particles leaving the simulation box did so through the top boundary, meaning that they are either sputtered atoms from the surface or reflected incident particles.

MD simulations were performed with a material having a surface four times larger (108,000 atoms) or twice deeper (54,000 atoms) to confirm that the use of a larger material gives essentially the same sputtering yields. The material was initially thermalised at the normalised temperature $\bar{T} = k_B T / 4\varepsilon = 0.006$, with k_B being the Boltzmann constant and T being the material temperature. For a typical material with $\varepsilon = 1$ eV, this normalised temperature corresponds to a temperature $T = 300$ K.

At the beginning of each injection cycle, a single atoms was injected with an normalised incident energy $\mathcal{E}$ at normal incidence, i.e., along the z axis. The simulation was performed with a normalised timestep $\bar{\delta}t = 1.7 \times 10^{-3}$, which corresponds to a timestep in physical units $\delta t = 0.1$ fs for a material with $m = 58.693$ g mol⁻¹ (corresponding to the mass of Ni), $\sigma = 1.5$ Å and $\varepsilon = 1$ eV. Up to $\tau = 12.0$, constant-energy conditions (NVE) were applied. From $\tau = 12.0$ to $\tau = 30.8$, a Langevin cooling²² was applied, followed by the application of constant-temperature conditions (NVT) between $\tau = 30.8$ and $\tau = 34.2$ to force the system to reach a thermalised state at $\bar{T} = 0.006$. The relaxation of the system after a single ion bombardment would take much longer time in real materials. The damping parameter (i.e., inverse of the normalised friction coefficient) τ_{damps} and the target temperature $\bar{T}$ of the Langevin cooling were $\tau_{\text{damp}} = 17.1$ and $\bar{T} = 0.006$. At the end of the cycle, i.e., at $\tau = 34.2$, all atoms out of interaction with the substrate bulk are considered as sputtered atoms and removed from the simulation to avoid the accumulation of floating atoms above the substrate.

This injection cycle was repeated around 1,000 times (i.e, around 1,000 injec-

tions or a normalised ion dose of 1.87) until the sputtering yield reached steady state, i.e., became independent of the ion dose. A summary of the simulation parameters with the corresponding dimensional values is given in Table IV-1. The substrate used in this study is represented in Fig. IV-3a.

Table IV-1 – Summary of the simulation parameters used in this study. Quantities in physical units are given for $m = 58.8 \text{ g mol}^{-1}$ (i.e., the atomic mass of Ni), $\varepsilon = 1 \text{ eV}$, and $\sigma = 1.5 \text{ \AA}$.

Parameter	Quantity	
	Normalized	Physical
Timestep $\delta\tau$	1.70×10^{-3}	0.1 fs
Ion dose	1.87	$8.31 \times 10^{15} \text{ cm}^{-2}$
Target temperature $\bar{T}_{\text{target}}$	6.5×10^{-3}	300 K
Langevin thermostat damping parameter τ_{damp}	17.1	1.1 ps
Time for NVE simulation	0.0 to 12.0	0.0 ps to 0.7 ps
Time for Langevin thermostat	12.0 to 30.8	0.7 ps to 1.8 ps
Time for NVT simulation	30.8 to 34.2	1.8 ps to 2.0 ps

IV.3 Simulation results

IV.3.1 Sputtering yield

As mentioned earlier, the sputtering yield Y of surface atoms of species α is defined as the average number of atoms of species α removed from the material per ion impact, i.e.,

$$Y = \frac{N_{\alpha}^{\text{gas}}}{N_{\beta}^{\text{in}}}$$

with N_{α}^{gas} and N_{β}^{in} denoting the total number of atoms of species α removed from the material surface (and therefore in the gas phase) and the number of incident ions of species β . The sputtering yield is usually measured in steady state, i.e., when Y averaged over a certain period of ion incidence hardly depends on the ion dose.

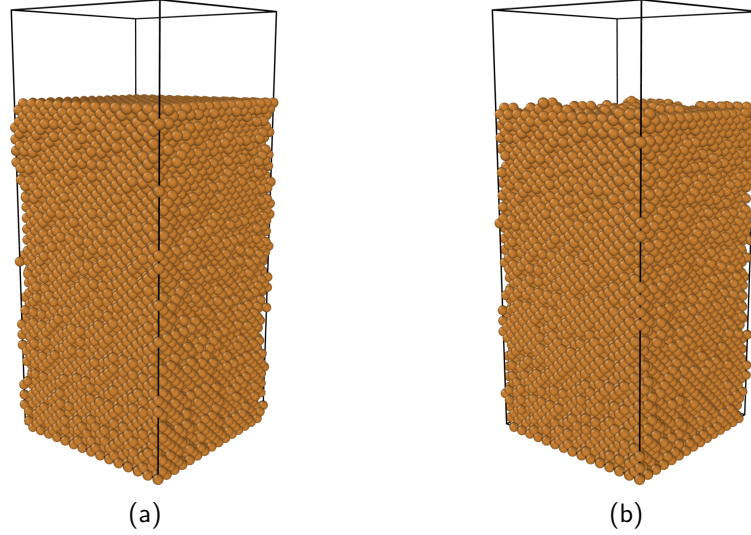


Figure IV-3 – Three-dimensional representation of the LJ material used for this study. Small sphere represent LJ particles and the black frame represent the simulation box. No incident particle is seen in (b), which is typical because all incident particles interact with other particle only repulsively. Periodic boundary conditions are applied in the horizontal directions, so that the top surface represent an infinitely wide surface. (a) Initial material model with the (100) top surface, which consists of 27,000 particles. (b) Material model after the injection of 1,000 LJ particles (normalised ion dose of 1.87) with a normalised incident energy $\mathcal{E} = 250$ for $\mu = 0.68$ and $\rho = 1.06$. The angle of incidence is normal to the surface. Both material models are in thermal equilibrium at a normalised temperature $\bar{T} = 0.006$.

If the incident ions are of the same species as surface atoms, the experimentally measured sputtering yield (i.e., self-sputtering yield) is defined differently because the incident and surface species cannot be distinguished experimentally. The self-sputtering yield Y_{self} is defined¹³⁴ as

$$Y_{\text{self}} = \frac{N_{\text{all}}^{\text{gas}}}{N_{\text{in}}}$$

with $N_{\text{all}}^{\text{gas}}$ and N_{in} denoting the total number atoms removed or reflected from the material surface and the number of incident ions during a certain period of ion incidence when the system is in steady state. It should be noted that, if $Y_{\text{self}} < 1$, the net deposition takes place even if surface atoms are sputtered by the impact of incident ions.

If the material species (α) and incident species (β) are the same, the relation between Y and Y_{self} may be given formally as

$$Y_{\text{self}} = \frac{N_{\alpha}^{\text{gas}} + N_{\beta}^{\text{gas}}}{N_{\beta}^{\text{in}}} = Y + (1 - s) \quad (\text{IV-5})$$

with N_{β}^{gas} denoting the total number atoms of species β desorbed or reflected from the material surface and $s = 1 - N_{\beta}^{\text{gas}}/N_{\beta}^{\text{in}}$ being the sticking probability of the incident species. Most self-sputtering cases that we are interested in are those of stable solid materials such as metal. In such cases, energetic ions with normal incidence typically penetrate deeply into the material and get deposited, so their sticking probability is close to unity, i.e., $s \simeq 1$ and sputtered species are mostly surface atoms. Therefore, the sputtering yield of surface atoms Y is essentially equal to the self-sputtering yield Y_{self} . However, when the incident energy is low or the angle of incidence is large from the surface normal, the sticking probability s becomes small and the difference between Y_{self} and Y can become significant.

Furthermore, in our system of Eq. (IV-4), the incident atoms only have repulsive potential and therefore cannot be the same as the material atoms even with parameters of $\mu = 1$ and $\rho = 1$. However, as discussed above, if the incident energy is sufficiently high and the injected atoms are embedded in a deeper region of the material, we expect the yield Y of sputtered species from the surface is comparable with the self-sputtering yield Y_{self} of the full LJ system¹³⁴ because the repulsive potential is similar. A more detailed discussion is found in Appendix C.2.

IV.3.2 Energetic dependency

MD simulations were performed to determine the dependence of the sputtering yield Y on the normalised kinetic energy $\mathcal{E}$. The angle of ion incidence was normal to the surface. The Fig. IV-4 shows the obtained physical sputtering yield for a couple of combinations of system parameters μ and ρ . We did not plot the yield for the energy higher than $\mathcal{E} > 10^3$ because, at such high energies, the sputtering yields obtained from the LJ system significantly deviate from those of the real materials and the correction of the repulsive potential would be needed to simulate the real system.¹³⁴

It is seen that the sputtering yield increases with the normalised energy $\mathcal{E}$ and is similar to those with different parameters in an energy range of around $\mathcal{E} > 200$. The dotted lines are fitting curves to the experimentally observed sputtering yields of Ni by Ne, Ni, and Xe ions. The comparison with such experimental values will be discussed in Sect. IV.3.4. The parameters μ and ρ selected here also correspond to those of the actual systems, as will be discussed in Sect. IV.3.4.

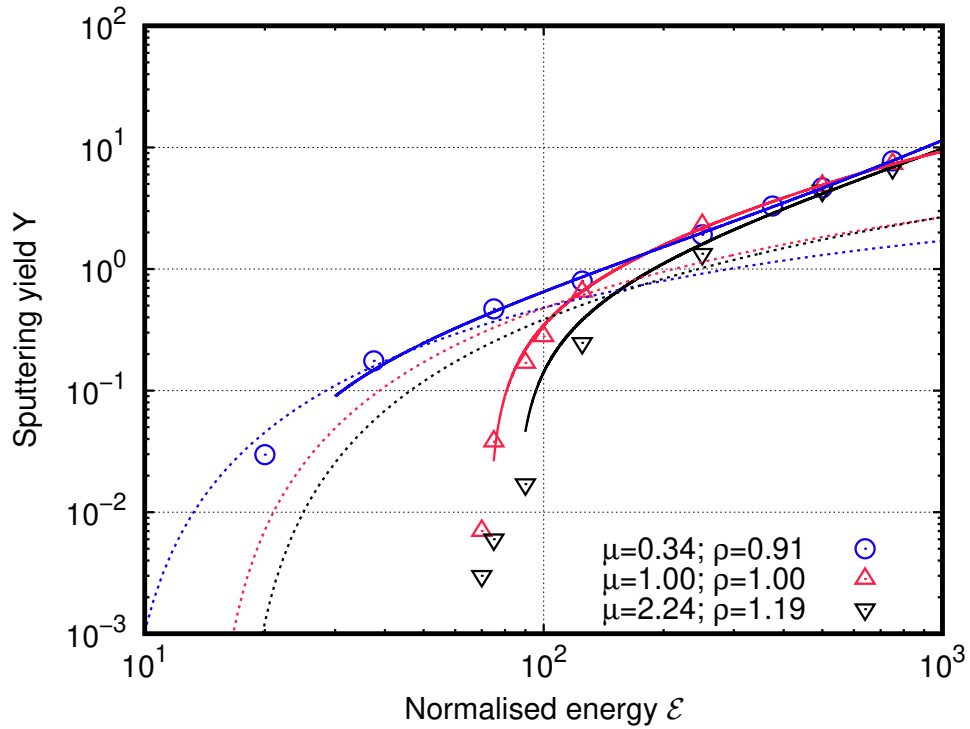


Figure IV-4 – Sputtering yields of surface atoms Y with respect to the normalised energy $\mathcal{E}$ for different sets of the system parameters. The circles, up-pointing triangles, and down pointing triangles are for $(\mu, \rho) = (0.34, 0.91)$, $(1.00, 1.00)$, $(2.24, 1.19)$, which correspond to the sputtering of Ni by Ne⁺, Ni⁺, and Xe⁺ ions, respectively. The blue, red, and black dashed curves are the empirical fitting functions by Yamamura and Tawara⁵⁷ for experimentally obtained sputtering yields of Ni by Ne⁺, Ni⁺, and Xe⁺ ions. It should be noted that the red curve represents the self-sputtering yield Y_{self} of Ni, rather than the sputtering yield of surface atoms Y .

IV.3.3 Dependence on parameters μ and ρ

The dependence of sputtering yield on the two parameters μ and ρ at $\mathcal{E} = 250$ is shown in Fig. IV-5. The angle of ion incidence was normal to the surface. The filled circle, filled up-pointing triangle, and filled down-pointing triangle of this figure are the cases corresponding to the data plotted in Fig. IV-4. The corresponding experimental values are plotted with crosses, which will be discussed in Sec. IV.3.4.

It is seen that the yield value Y varies up to an order of magnitude as ρ increases from 0.33 to 2. More specifically, for each value of μ , as ρ increases, the sputtering yield of surface atoms Y increases until it reaches its maximum and then decreases. In other words, if the incident ion is too small compared with the interatomic distance of the material surface (e.g., $\rho < 0.5$), the sputtering yield is low probably because the incident ions penetrate the material too deeply and release its energies and momenta along longer collision paths, making the energy and momentum transfer to each surface atom less efficient. On the other hand, if the incident ion is too large (e.g., $\rho > 1.2$), the sputtering yield is again low probably because the incident ions cannot penetrate the material deeply.

It is also seen in Fig. IV-5 that the yield Y is the largest around $\mu = 1$ and $\rho = 1$ possibly because the momentum transfer among atoms with the same mass and size is the most efficient. However, this observation is not universal and depends on the incident energy, as we see in Fig. IV-4, where the sputtering yield for $\mu = 0.34$ and $\rho = 0.91$ is the highest among the three cases in an energy range of $\mathcal{E} < 100$. In general, if the value of μ is extremely small (e.g., $\mu < 1$), the sputtering yield is also extremely small as light ions cannot transfer much energy or mass in a single impact.

IV.3.4 Comparison with experiments

So far we have evaluated the sputtering yield for a range of μ and ρ without reference to real materials. For real materials with specific incident ions, these two parameters are not independent. For example, for smaller incident ions, both mass ratio and relative interaction range are typically small. In this subsection, we discuss how these parameters can be set for real materials.

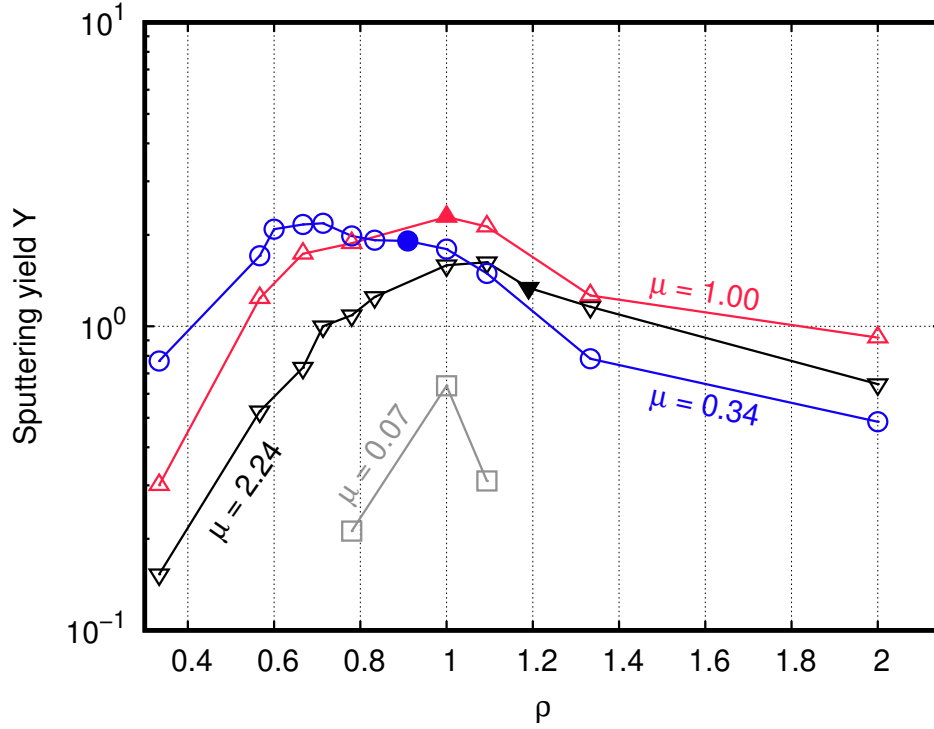


Figure IV-5 – Sputtering yield of surface atoms Y with respect to ρ for several values of μ . The filled circle, filled up-pointing triangle and filled down-pointing triangle correspond to the sputtering yields also shown in Fig. IV-4. The experimentally obtained yields of Ni by Ne^+ , Ni^+ and Xe^+ ions from Ref. 57 are shown with blue, red, and black crosses, respectively. It should be noted that the red cross represents the self-sputtering yield Y_{self} . The lines are to guide the eye.

One can determine ε and σ of the LJ potential from the basic properties of a solid that the corresponding atoms constitute, especially if the solid is a face-centered cubic (fcc) crystal that the LJ particles are known to form under low-temperature and low-pressure conditions.

The parameter σ can be calculated from the closest neighbour distance d , which is known for most materials.⁴³ For an fcc crystal, the closest neighbour distance d , the lattice constant l_a , and σ are related by

$$d \simeq 0.71l_a \simeq 1.1\sigma \quad (\text{IV-6})$$

The parameter ε can be obtained from the cohesive energy E_C , which is defined

as the energy per unit amount of substance needed to separate all the constituent atoms into non-interacting neutral atoms. The cohesive energy is also known for most materials.⁴³ The cohesive energy E_C of an fcc crystal and ε are related by

$$E_C = -8.6\varepsilon \quad (\text{IV-7})$$

Both relations (IV-6) and (IV-7) are in good agreement with previous calculations.¹¹⁶

For simplicity, we extend these definitions of σ ε for any material (even if it does not form an fcc lattice) for which the closest neighbour distance d and cohesive energy E_C are defined. It is understood that, with such extended definitions of σ and ε , the actual atomic interaction for some materials may not be well represented by the LJ potential. The parameters σ and ε determined in this way for various gaseous and material species are listed in Table IV-2. (These parameters of gaseous species at standard temperature and pressure were determined from their solid states at sufficiently low temperature.)

Table IV-2 – Values of the LJ parameters σ and ε evaluated with Eqs. (IV-6) and (IV-7) in this work and quoted from literature.

Species	This work		Literature		
	σ (Å)	ε (eV)	σ (Å)	ε (eV)	References
He	2.56	8.74×10^{-4}	2.56	8.74×10^{-4}	43
C	1.42	8.61×10^{-1}	—	—	—
Ne	2.90	2.34×10^{-3}	2.74	3.12×10^{-3}	43
Al	2.62	3.96×10^{-1}	2.62	3.94×10^{-1}	137
Si	2.15	5.41×10^{-1}	—	—	—
Ar	3.45	9.35×10^{-3}	3.40	1.04×10^{-2}	43
Fe	2.27	5.19×10^{-1}	2.32	5.19×10^{-1}	137
Ni	2.28	5.19×10^{-1}	2.28	5.19×10^{-1}	137
Cu	2.37	4.08×10^{-1}	2.34	4.08×10^{-1}	137
Kr	3.67	1.36×10^{-2}	3.65	1.40×10^{-2}	43
Xe	3.98	1.87×10^{-2}	3.98	2.00×10^{-2}	43
Au	2.64	4.45×10^{-1}	2.64	4.44×10^{-1}	137

For interactions between atoms of different species, the values of σ and ε may

be estimated from those parameters of each species. In this study, we use the following mixing rules, the Lorentz rule¹³⁸ for σ and the Berthelot rule¹³⁹ for ε ;

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$

Tables IV-3 and IV-4 show the values of the mass ratio μ and relative interaction range ρ obtained from the Lorentz-Berthelot combining rules above with the parameters listed in Table IV-2 for the interaction of materials C, Al, Si, Fe, Ni, Cu and Au with incident ionic species of He, Ne, Ar, Kr and Xe.

Table IV-3 – Mass ratio μ for combinations of surface materials and incident species.

Surface material	Incident species				
	He	Ne	Ar	Kr	Xe
C	0.33	1.68	3.33	6.98	10.93
Al	0.15	0.75	1.48	3.11	4.87
Si	0.14	0.72	1.42	2.98	4.67
Fe	0.07	0.36	0.72	1.50	2.35
Ni	0.07	0.34	0.68	1.43	2.24
Cu	0.06	0.32	0.63	1.32	2.07
Au	0.02	0.10	0.20	0.43	0.67

The correlation between the parameters μ and ρ is seen in Fig. IV-6, where the values of ρ and μ in Tables IV-3 and IV-4 are plotted. It is seen, while μ varies by nearly three orders of magnitude, the variation of ρ is rather limited. The correlation is nearly linear as indicated by the dotted curve.

By comparing Fig. IV-6 with the sputtering yields summarized in Fig. IV-5, we observe that the sputtering yield indeed depends strongly on these parameters in general. However, if we confine our interest to materials of relatively large atomic masses (such as Al or larger) and exclude extremely light or heavy incident species relative to the mass of a surface atom (such as He for most surface materials or Xe for some light surface materials), the values of the parameters fall into the ranges of $0.3 < \mu < 3$ and $0.8 < \rho < 1.2$, as we see in Tables IV-3 and IV-4.

Table IV-4 – Relative interaction range of the incident ion ρ for combinations of surface materials and incident species. Typical crystalline structures of the surface materials are denoted in ().

Surface material	Incident species				
	He	Ne	Ar	Kr	Xe
C (diamond)	1.06	1.19	1.43	1.51	1.63
Al (fcc)	0.76	0.85	0.99	1.04	1.11
Si (diamond)	0.84	0.93	1.10	1.16	1.24
Fe (bcc)	0.82	0.91	1.06	1.12	1.19
Ni (fcc)	0.81	0.91	1.06	1.12	1.19
Cu (fcc)	0.80	0.90	1.05	1.10	1.18
Au (fcc)	0.76	0.84	0.98	1.03	1.10

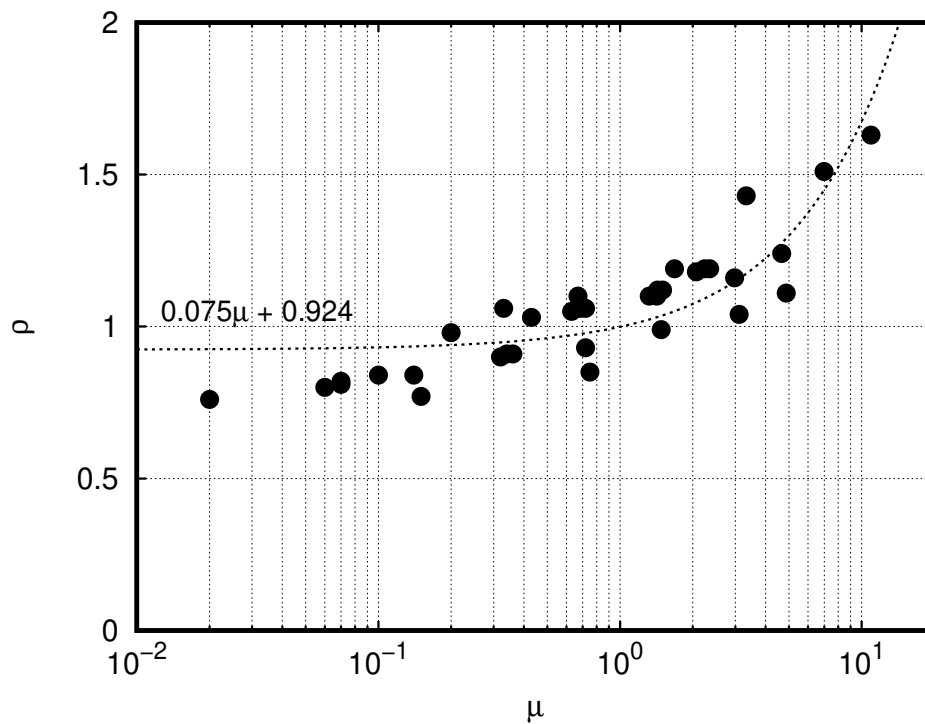


Figure IV-6 – Correlation between the relative interaction range ρ and the mass ratio μ given in tables IV-3 and IV-4. The dashed line is a linear fitting curve of $\rho = 0.075\mu + 0.924$.

Figure IV-5 shows that the sputtering yields at $\mathcal{E} = 250$ are relatively similar within this parameter range; although the μ varies by an order of magnitude in this range, the yield varies only up to a factor of 2.

In Fig. IV-4, the sputtering yields for $(\mu, \rho) = (0.34, 0.91)$, $(1.00, 1.00)$, and $(2.24, 1.19)$ correspond to those of Ni by Ne^+ , Ni^+ , and Xe^+ ions, according to Tables IV-3 and IV-4. The blue, red, and black dotted curves are the empirical fitting functions proposed by Yamamura and Tawara⁵⁷ for experimentally obtained sputtering yields of Ni by Ne^+ , Ni^+ , and Xe^+ ions. It should be noted that the red dotted curve represents experimentally obtained self-sputtering yields of Ni. The three curves take similar values in an energy range of $100 < \mathcal{E} < 1,000$ although their values are lower than the yield values of the LJ system. As discussed in Ref. 134, this is expected because the repulsive potential of the LJ system is too strong compared with those of actual atoms.

Figure Fig. IV-7 compares the sputtering yields of the LJ system obtained in this study with experimentally obtained sputtering yields of various materials. The LJ-based yield values obtained from MD simulations are the same as those plotted in Fig. IV-5 and their symbols are also the same. The experimental data were obtained from the empirical fitting functions by Yamamura and Tawara presented in Ref. 57. Especially, the experimental yield values of Ni by Ne^+ , Ni^+ , and Xe^+ ions are plotted by blue, red, and black crosses, whose values of μ are 0.34, 1.00 and 2.24, respectively. It is seen that these values are lower than the corresponding yield values of the LJ system.

Except for the experimental yield values of Ni by Ne^+ , Ni^+ , and Xe^+ ions mentioned above, no simulation data is presented with the same μ and ρ values as those of the corresponding experimental data. However, the mass ratios of the experimental data presented here mostly fall in the range of $0.3 < \mu < 3$ with a few exceptions. In most cases, the experimental values seem close to the corresponding simulation values within a factor of 2 to 3, except for Al and Si, whose yields are much lower than those of the corresponding LJ system. The mass ratio of Al to Kr^+ or Xe^+ is larger than 3 and Si has diamond crystalline structure, which may partially account for the discrepancies. For each material, however, we observe the weak dependence of the yield on the mass ratio μ , which varies more than a factor 7 in this figure.

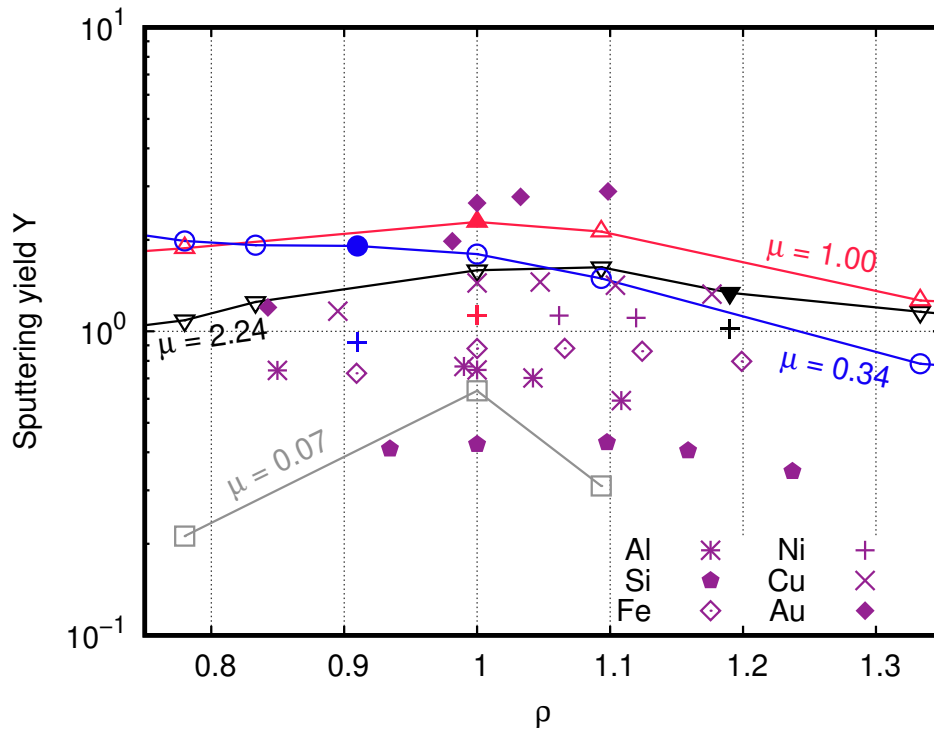


Figure IV-7 – Comparison of the sputtering yields obtained from MD simulations of this study with experimentally obtained sputtering yields at $\mathcal{E} = 250$ as functions of the relative interaction range ρ . The simulation values are the same as those plotted in Fig. IV-5 and their symbols are the same. The experimentally obtained yields of Al, Si, Fe, Ni, Cu, and Au are denoted by the symbols listed in the legends. For each material, from left to right, the experimentally obtained sputtering yields by Ne^+ , Ar^+ , Kr^+ , and Xe^+ are plotted, except for the self-sputtering at $\rho = 1$. Among them, the experimentally obtained yields of Ni by Ne^+ , Ni^+ , and Xe^+ ions are shown with blue, red, and black crosses, whose values of μ are 0.34, 1.0 and 2.24, respectively. The corresponding yields obtained from the LJ-based simulations are plotted by the filled blue circle, filled red up-pointing triangle, and filled black down-pointing triangle, as in Fig. IV-5. It should be noted that the red cross represents the self-sputtering yield Y_{self} . All experimental data were obtained from the empirical fitting functions by Yamamura et Tawara.⁵⁷

Figure IV-4 also shows that, in a lower energy range of $\mathcal{E} < 100$, the sputtering yields of these three cases obtained from MD simulations deviate from each other and so do the three dotted curves. It is seen that the circles follow the corresponding experimental curves. The predicted sputtering yields of Ni by Ni^+ , and

Xe^+ ions deviate significantly from the experimental curves. As discussed earlier, the sputtering yield Y plotted here is different from the self-sputtering yield Y_{self} , which the red dotted curve represents. The disagreement between the red dotted curve and red up-pointing triangles may arise from this difference in definition. For more discussion on this, the reader is referred to Appendix C.2. The discrepancy between the black dotted curve and black down-pointing triangles, referring to the sputtering yield of Ni by Xe^+ ions, especially at low energies, is not clear. When the incident ion energy is low, the sputtering yield may depend more sensitively on the details of actual atomic interactions.

IV.4 Conclusion

We evaluated sputtering yields of the (100) surface of an fcc solid whose atoms interact with the LJ potential subject to the bombardment of ions that interact with surface atoms with LJ-type repulsive potential, using MD simulation. No Coulomb interaction was taken into account in this model because, in real systems, incident ions are expected to be charge-neutralized by an Auger emission process right before they impact the surface.¹³⁵ The equations of motion solved in this study are given by Eq. (IV-4) in the normalized form and the system depends only on two parameters, i.e., the ratio of the incident ion mass to the mass of surface atom μ and the relative interaction range of the incident ion ρ .

This study is essentially an extension of an earlier study of Ref. 134 on the self-sputtering of the LJ system. In Ref. 134, the incident species are assumed to be the same as those of the surface atoms and obey the full LJ potential whereas, in the present study, the incident species have only repulsive interactions with surface atoms. Therefore, strictly speaking, the system of this study does not include that of Ref. 134. However, as the repulsive potential of energetic incident species, rather than their attractive interactions with surface atoms, is expected to affect the collision cascade dominantly, the average number of surface atoms ejected from the surface by knock-on collisions should be similar between the two systems.

Using the LJ system for two species defined above, we evaluated the sputtering

yields by MD simulations. In the energy and parameter range we examined, i.e., $10 < \mathcal{E} < 1,000$, $0.07 \leq \mu \leq 2.24$, and $0.33 \leq \rho \leq 2$, the sputtering yield vary by orders of magnitude. As well known from earlier studies, the sputtering yield is an increasing function of the incident energy and varies up to 10 or more. In general, if the value of μ is extremely small (e.g., $\mu < 0.1$), the sputtering yield is also extremely small as light ions cannot transfer much energy or momentum to the surface in a single impact. For a given incident energy $\mathcal{E}$ and a mass ratio μ , as the incident ion becomes smaller or larger than certain values (e.g., $\rho < 0.5$ or $\rho > 1.2$), the sputtering yield becomes lower. This is probably because, if the radius of incident ions is too small, they penetrate the material too deeply and release their energy and momentum along longer collision paths, thus making the energy and momentum transfer to each surface atom less efficient. If the radius is too large, they cannot penetrate the material deeply, thus mostly affecting only the top surface atoms they collide with.

The goal of this study is to explain why physical sputtering yields tend to have weak dependence of the mass of incident ions except for extremely light ions such as He^+ . This is generally the case when the incident energy is less than a couple of thousands eV, i.e., the energy range of interest for semiconductor device manufacturing processes. If the incident ion energy is low and the sputtering yield is less than 0.1, the sputtering yield seems to depend on the mass of incident species more strongly, but the yield is so small and the difference among small yields hardly matters in most practical applications. To determine the system parameters μ and ρ of the LJ system most relevant for real materials, we used Eqs. (IV-6) and (IV-7) as well as the Lorentz-Berthelot combining rules. For real physical systems, the values of μ and ρ have a strong correlation. It was found that, for the combination of materials and ions of our interest (excluding extremely light ions), the set of parameters μ and ρ falls into a narrow range of around $0.3 < \mu < 3$ and $0.8 < \rho < 1.2$. The MD simulations of this study have shown that the sputtering yields are relatively similar in this parameter range. Although the μ varies by an order of magnitude in this range, the yield varies only up to a factor of 2. This accounts for the similarity of sputtering yields among different incident ion species.

Admittedly, how similar or different the sputtering yields among different in-

cident ionic species are rather subjective. As we seen in Fig. IV-1 and discussed above for the LJ system, the sputtering yield does depend rather strongly on the mass of mass of incident energy on the high or low ion-incident-energy ranges. Probably because for most processing applications, we use the ion incident energy ranging from around 100 to a few thousands eV and care less about the extremely low sputtering yields, we might have formed a rather biases impression that the sputtering yield is less dependent on the mass of incident ions, What we have clarified in this study using the LJ system is that, as emphasised above, in the limited parameter range of around $0.3 < \mu < 3$ and $0.8 < \rho < 1.2$, the sputtering yield varies within a factor of 2 or so.

Concerning the discussion above, another general trend that we may find in Fig. IV-1 is that, for each surface material, the sputtering yield by heavier ions is higher at high ion incident energy and lower at low ion incident energy, Even for extremely light He^+ ions, its sputtering yields are close to those by heavier ions at low ion incident energy. Except for He^+ ions the sputtering yields by heavier ions overtake those by lighter ions in the intermediate energy range as the ion incident energy increases. This means that the sputtering yields by most ions are nearly equal in the intermediate ion-incident-energy range, which we have attempted to explain in this study, A similar trend is seen in Fig. IV-4, where the sputtering yields by heavier ions are shown to be much lower than those by lighter ions at $\mathcal{E} < 100$ for the LJ system. The reason for this trend is not clear and left as a subject of future work.

How representative the LJ system is of real systems is another question. It has been known that the repulsive potential of the LJ system is much stronger than those of real atoms,^{111,134} which tends to give unrealistically high sputtering yield at high ion incident energies. This is the reason that, in this study, we focused our study on a normalised energy range of $\mathcal{E} < 1,000$, which corresponds to an energy range of less than a couple of thousands eV in physical units. Even in this range, we tend to overestimate the sputtering yield of real systems with our LJ model. However, in this study, we attempt to understand the qualitative nature of sputtering and therefore defer discussion on the validity of the LJ's repulsive potential to a future study.

A recent study¹⁰⁷ showed that, based on analysis of a large amount of experi-

mentally obtained sputtering yield data, the sputtering yield and related properties depend essentially on a relatively small number of physical parameters. In other words, the sputtering yield may not depend sensitively on the details of interatomic potentials. Based on this premise, we surmise that the present study based on the LJ system has captured some essence of the sputtering properties of real materials.



Evaluation of nickel self-sputtering

As the dimensions of semiconductor devices continue to diminish and complex three-dimensional structures and novel non-silicon-based materials are introduced to the advanced semiconductor device design,^{7,11} the manufacturing processes of such devices also face new technological challenges. Achieving damageless metal etching with atomic-scale accuracy is one of such challenges. For example, the formation of a magnetic tunnelling junction (MTJ) of a magnetoresistive random access memory (MRAM) device¹⁴⁰ requires an etching technique that does not damage the functionality of the MTJ. Unlike etching processes of Si-based materials or compound semiconductors, which typically use surface chemical reactions to form volatile species, conventional dry etching processes of metals mostly rely on physical sputtering. This is because few chemical reactions have been found to form highly volatile compounds on a metal surface.

The ultimate goal of this research is to assess the possibility of establishing a reactive ion etching (RIE) of metals in general, using surface chemical reactions that form volatile metal compounds at relatively low surface temperature.^{141–143} In RIE or plasma etching processing,^{6,8–10,13} chemically reactive species generated in a plasma tend to adsorb on the material surface and surface chemical reactions are initiated by energy supplied by plasma-generated energetic ions impacting on the surface. Dynamical effects of ion impact on the surface, i.e., physical sputtering,^{45,46} constitute one of the most fundamental components of a dry etching

process.

Therefore, in this study, we examine self-sputtering processes of nickel (Ni) as the first step to understand possible RIE of metals in general. Ni was selected as a sample material of ferromagnetic metal although, in standard MRAMs, more complex ferromagnetic alloys such CoFeB are widely used. One of the advantages of studying Ni is that its sputtering properties were extensively studied in the past and a wealth of experimental data is now available for Ni.^{57,144–146}

Self-sputtering of a single-element material is the simplest system to study as the phenomena is governed by the atomic interactions of single species only. Therefore molecular dynamics (MD) simulations^{147,148} should unveil the essential properties of the self-sputtering of a material if one uses a sufficiently accurate description of its atomic interactions. Indeed, Hanson *et al.*¹⁰³ evaluated Ni and aluminium (Al) self-sputtering yields, using classical MD simulations. The ion incident energy examined in the study was relatively low, i.e., from 25 eV to 500 eV. The obtained yield values were slightly higher in general than the corresponding experimental values^{144,146} but they were overall in good agreement. More recently, Metspalu *et al.* evaluated the self-sputtering yield of Cu in an energy range from 0.1 eV to 5,000 eV, using classical MD simulation.¹⁰⁵ The obtained yield values were slightly higher in general than the experimental values suggested by Yamamura and Tawara’s fitting curve,^{57,145} but the overall agreement was reasonable.

Classical MD simulations, where the motions of atoms interacting among themselves are analyzed dynamically with the predetermined interatomic potential models, has been used to study beam-surface interactions since the early 1980s. Unlike binary-collision models,^{30,86,87} MD simulation can self-consistently model multi-body collisions, which play the dominant role when atoms with relatively low kinetic energies collide with other atoms in a material. The sputtering phenomena first studied by classical MD simulation were those for metals,^{42,101–105,149–157} which have been a topic of interest since the 1940s. As the dry etching process technologies for semiconductor manufacturing applications have gained much attention, classical MD simulations have also been used extensively to analyze beam/plasma-surface interactions for Si- and carbon (C)-based materials.^{37,88–95,97–99,129,158–163}

The ion-beam studies provide a wide range of experimental data on sputtering phenomena, including the determination of sputtering yields.⁵⁶ The data obtained

from such experiments may be directly compared with MD simulation results. Extensive experimental studies on sputtering using well-controlled ion beams have been performed for metals,^{70,71,144,146,156,164–169} metal oxides,^{72–77,85} and Si- and C-based materials.^{56,58–60,63,64,68,82,83}

In this study, we performed classical MD simulations to study Ni self-sputtering. Our specific interest was to show how the selection of interatomic potential models could affect the sputtering yields obtained from such simulations. To achieve this goal, we selected two existing interatomic potential models for Ni that were designed to reproduce material properties of Ni in thermodynamic equilibrium and compared the sputtering yields evaluated by MD simulations based on those potential models with the existing experimental data. In the case of high ion-incident energy, where incident ions and recoil atoms may collide with other atoms in the material at very short distances, the repulsive interactions at short interatomic separations of Ni atoms are expected to play an important role in determining the sputtering phenomena. Such short-range interactions are typically not taken into account in standard interatomic potential models designed for systems in thermodynamic equilibrium. Therefore we also modified the short-range repulsive interactions such that the sputtering yields obtained from MD simulations agreed well with experimentally obtained values.

The chapter is structured as follows: In Sect. V.1, the simulation method is discussed and in Sect. V.2, the models of atomic interactions, especially those based on the Embedded Atomic Method (EAM) are presented. MD simulation results are given and compared with experimental data in Sect. V.3.

V.1 MD simulation

In this study, classical MD simulations were used to evaluate self-sputtering yields of Ni. In classical MD simulations, Newton's equation of motion for each atom is solved numerically for given interatomic potential functions or forces. The interatomic potential functions used in this study will be discussed in the following section. All MD simulations presented in this study were performed with LAMMPS.^{114,136} LAMMPS is an open-source code distributed under the terms of

the GNU General Public License (GPL) by Sandia National Laboratories, USA.

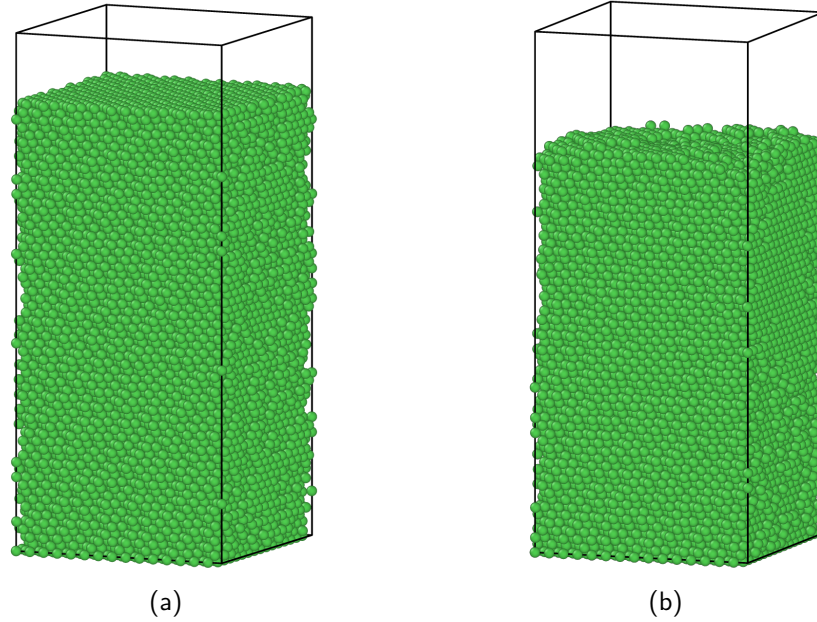


Figure V-1 – Three-dimensional representations of a typical Ni substrate used in this study. Each green sphere represents a Ni atom and the black frame represents the simulation box. The periodic boundary conditions are imposed in the horizontal directions, so that the top surface represents an infinitely wide surface. (a) The initial substrate whose top surface is (100), consisting of 27,450 Ni atoms. (b) The Ni substrate after 2,000 Ni ion injections (an ion dose of $7.1 \times 10^{15} \text{ cm}^{-2}$) with an incident energy of 1,000 eV. Both substrates are in thermal equilibrium at 300 K.

To emulate the beam experiments of Ni self-sputtering, Ni^+ ions were injected into a Ni surface one by one at random locations of impact with a given incident ion energy and a fixed angle of incidence. In the simulation, the substrate material was represented by a collection of Ni atoms arranged in the face-centered cubic (fcc) lattice with a lattice parameter of $a = 3.524 \text{ \AA}$. A typical Ni substrate material used in this study is shown in Fig. V-1a, which consists of 27,450 Ni atoms and whose horizontal dimensions and depth are $5.3 \text{ nm}^2 \times 5.3 \text{ nm}^2$ and 10.6 nm with a (100) top surface. We also performed MD simulation with Ni substrates of different sizes and surface orientations such as (110) and (111). In this study, we focused mostly on the substrate with a (100) top surface.

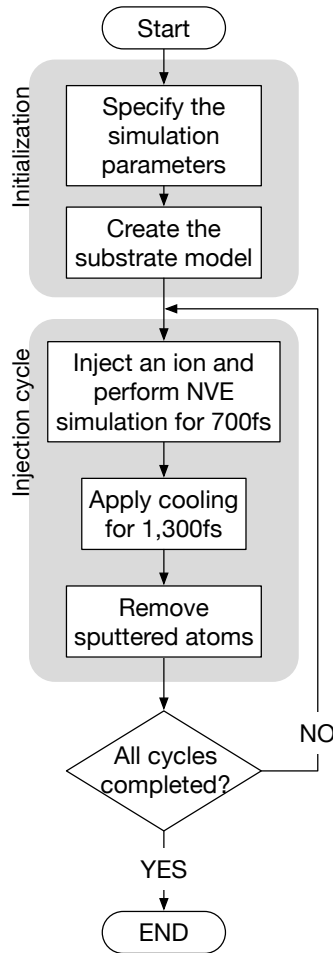


Figure V-2 – Flow chart of the MD simulation used in this study.

The rectangular solid of a Ni substrate was placed at the bottom of a rectangular simulation box, whose horizontal dimensions were the same as those of the solid. The height of the simulation box was 12.3 nm. The periodic boundary conditions were imposed in the horizontal directions, so that the rectangular solid of Fig. V-1a represented an infinitely wide slab. Its thickness, i.e., the depth, was also taken deep enough, so that the injected ions did not pass (or hardly passed) through the bottom of the simulation box. Therefore, the material model represented a sufficiently wide and thick metallic Ni substrate with the (100) surface. The atoms in a few atomic layers at the bottom of the substrate were fixed in position to prevent the substrate from moving downward by ion impact on the top surface. Atoms leaving the top or bottom surface of the simulation box were considered to be lost and removed from the system. Since the substrate was deep enough, all atoms that left the system did so through the top surface of the simulation box, which means they were either sputtered atoms from the surface or reflected incident ions. The Ni substrate model after 2,000 Ni ion injections, which corresponds to an ion dose

of $7.1 \times 10^{15} \text{ cm}^{-2}$, with an incident energy of 1,000 eV is shown in Fig. V-1b.

To ensure that we used a sufficiently large substrate to represent a realistic Ni surface, we also performed MD simulations using a twice deeper substrate with 54,450 Ni atoms as well as a substrate with 4 times larger horizontal area consisting of 109,800 Ni atoms and confirmed that the sputtering yields obtained from MD simulations with those larger substrates were essentially the same as those that we obtained using the substrate model of Fig. V-1a.

The flow of the MD simulation is summarized in Fig. V-2. The substrate was

initially thermalized at 300 K. Then a single Ni^+ ion was injected into the top surface of the substrate at $t = 0$ with a given incident energy at a random location of impact on the surface. The angle of incidence was set normal to the top surface unless stated otherwise. The MD simulation was performed under the constant total-energy (NVE) conditions for the first 700 fs. The time step used to integrate the equations of motion was 0.1 fs. After this, a Langevin cooling²² was applied for 1,300 fs to emulate slow-cooling and thermalization processes to force the system to reach a thermalized state at 300 K, which in reality would take place on much longer timescales. The target temperature and damping parameter (i.e., inverse of the friction coefficient) of the Langevin thermostat used in this study were 300 K and 1 ps. At $t = 2$ ps, all desorbed atoms from the surface (i.e., atoms not bonded with the substrate) were removed from the system and a cycle of single ion injection was completed. This cycle was repeated many times until the average number of sputtered atoms per ion injection reached steady state, i.e., became independent of the ion dose. In this study, the cycle was typically repeated 2,000 times (i.e., 2,000 atomic injections or an ion dose of $7.1 \times 10^{15} \text{ cm}^{-2}$). It should be noted that the surface roughness due to the ion bombardment also reached steady state after sufficient ion dose, as seen in Fig. V-1b.

The interatomic potential functions for ions are assumed to be the same as those for charge-neutral atoms for the sake of simplicity. In a typical beam experiment, the Ni metal surface is grounded such that the metal surface is not charged despite the fact that the incident ion beam supplies positive charges to the substrate surface. The incident Ni ion is also considered to be charge-neutralized right before it impacts on the substrate Ni surface owing to an Auger emission process.

V.2 Interatomic potential models

V.2.1 Embedding-Atom-Method (EAM) potential functions

The Embedding-Atom-Method (EAM) potential functions^{39,40} have been widely used to present the interatomic interactions of metals and metal alloys. Most of them are designed to reproduce mechanical and thermodynamic properties of specific metals but may not be able to reproduce their sputtering properties correctly.

In general, the mechanical and thermodynamic properties of a material are determined by the interactions of atoms around their equilibrium positions whereas the sputtering properties may be strongly influenced by the atomic interactions at short distances (e.g., nuclear-nuclear collisions) or the distances for bond breaking. In this study, we used a few different interatomic potential functions to represent Ni atoms in our MD simulations.

The total potential energy V of the system of N atoms of the same kind in the ground state may be given as:

$$V = \sum_{i=1}^N V_i(r_{i1}, r_{i2}, \dots, r_{i \ i-1}, r_{i \ i+1}, \dots, r_{iN})$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here $\mathbf{r}_i$ denotes the position of the i -th atom.

For an EAM potential function, V_i has the form

$$V_i(r_{i1}, r_{i2}, \dots, r_{i \ i-1}, r_{i \ i+1}, \dots, r_{iN}) = F \left(\sum_{\substack{j=1 \\ (j \neq i)}}^N \rho(r_{ij}) \right) + \frac{1}{2} \sum_{\substack{j=1 \\ (j \neq i)}}^N \phi(r_{ij}) \quad (\text{V-1})$$

Here the function F is called the embedding energy, which means the energy required to embed an atom in the background density. The function $\phi(r_{ij})$ represents a pair potential between atoms i and j and the function $\rho(r)$ is a normalized density of the electron cloud belonging to an atom at a distance r measured from the location of the atom's nucleus.

One of such EAM potential functions to represent Ni used in this study is the potential model for a Fe–Cu–Ni alloy developed by Bonny *et al.*⁴² The Ni potential of this potential model is based on an earlier work by Voter *et al.*¹⁷⁰ This EAM potential model is listed as “FeCuNi.eam.alloy” in the potential directory of LAMMPS.¹¹⁴ The three constituting functions, i.e., pair potential ϕ , normalized density ρ , and embedding energy F , for this Ni EAM potential model are plotted in Fig. V-3. Note that F and ϕ are given in units of eV whereas ρ is dimensionless. In this article, we call this Ni potential model P1 for brevity.

It is known that the EAM potential P1 is not designed to represent a pure Ni metal; it is designed to represent Fe–Cu–Ni alloys in general and its use to

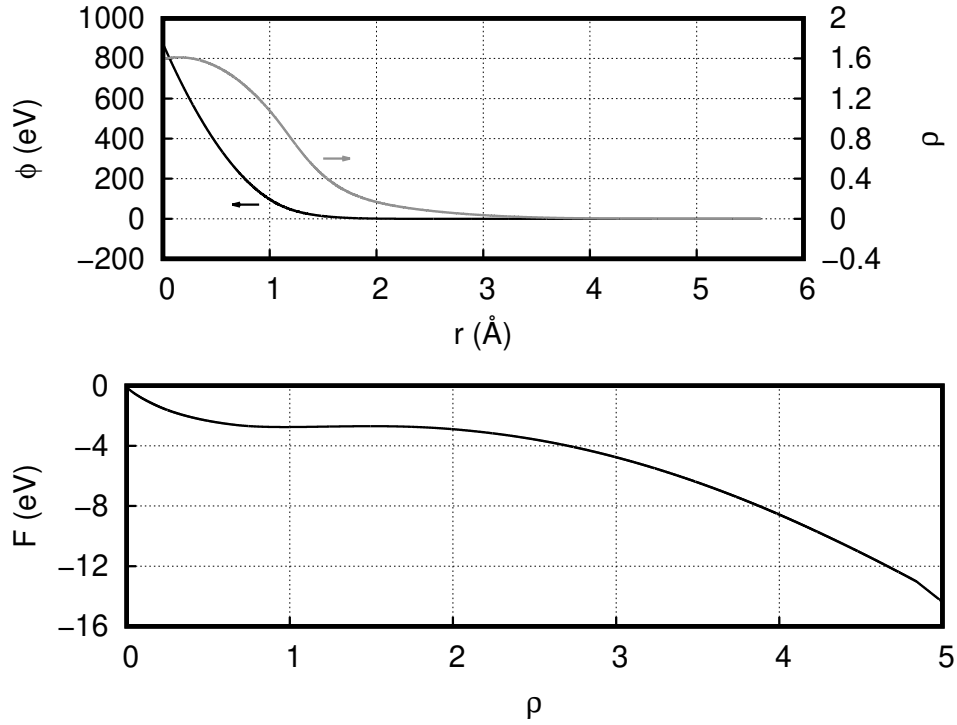


Figure V-3 – The three constituting functions for Ni EAM potential model P1 in this study, derived from the Fe–Cu–Ni EAM potential of Ref. 42. Here ϕ , ρ and F are the pair potential, normalized electronic density of a Ni atom, and embedding energy, respectively, as defined in Eq. (V-1).

represent a pure Ni metal is not indeed recommended. Nevertheless, the reason we selected model P1 as a base case in this study is that, among many existing EAM potential functions for Ni that we tested, MD simulations based on the potential model P1 provided some of the best Ni self-sputtering yields, i.e., yields closest to the corresponding experimental data. Furthermore, as seen in the following section, it also provides accurate values for some mechanical properties that we examined for a pure Ni metal. However, we by no means intend to imply that, therefore, the potential model P1 is the best EAM potential for Ni or Fe–Cu–Ni alloys in general. On the contrary, as we shall discuss later, a reliable potential function designed to represent mechanical and/or thermodynamical properties of a material may not be a good potential function to represent sputtering phenomena of the material. Another reason that we selected the potential model P1 is to

extend our study to sputtering of alloys in the future. Therefore, the selection of the potential model P1 in this study should be construed as nothing but a selection of one of many possible choices among well-studied EAM potential functions that can represent a pure Ni metal.

Another EAM potential model we used in this study is the one for Ni–Al–Co alloys developed by Purja Pun *et al.*,¹⁵³ which is listed in the NIST Interatomic Potentials Repository.²⁶ The three constituting functions for this Ni EAM potential model are plotted in Fig. V-4. In this article, we call this Ni potential model Q1. Although both P1 and Q1 are designed to model atomic interactions of Ni, the functional forms are very different, as seen in Figs. V-3 and V-4.

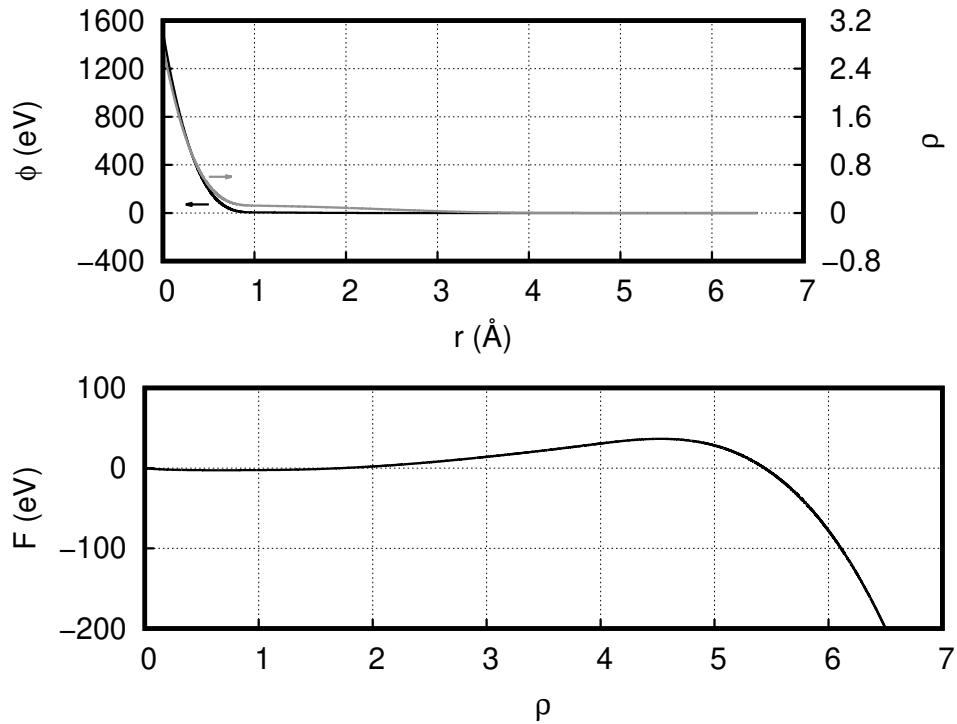


Figure V-4 – The three constituting functions for Ni EAM potential model Q1 used in this study, derived from the Ni–Al–Co EAM potential of Ref. 153. Here ϕ , ρ and F are the pair potential, normalized electronic density of a Ni atom and embedding energy, respectively, as defined in Eq. (V-1).

V.2.2 Short-range interaction

Many existing interatomic potential functions are designed to reproduce material properties in thermal equilibrium. However, high-energy phenomena, such as energetic atomic collisions and sputtering, may not be well reproduced by such potential functions. To reproduce sputtering phenomena properly by MD simulation, therefore, we must use interatomic potential functions that can reproduce atomic interactions for both high-energy collisions and motions near thermal equilibrium. Such functions may be obtained by modifying short-range interactions of existing interatomic potential functions designed for bulk materials in thermal equilibrium phenomena.

The Ziegler-Biersack-Littmark (ZBL) potential³⁰ is widely used to represent a short-range repulsive interaction among atoms. This function is defined for each pair of atomic species and has no adjustable parameter. It is typically not compatible with other interatomic functions at longer distances, including the EAM potential functions of Ni of our interest. Therefore, when the ZBL potential function is used for MD simulation on high-energy collision phenomena, it is smoothly connected with an interatomic potential function for longer interatomic distances by an empirical switching function. Stoller *et al.*¹⁰⁴ used various density-functional-theory (DFT) calculations to construct a repulsive pairwise potential function for Ni atoms that smoothly extends an interatomic potential function for a pure Ni metal to the ZBL potential for high-energy collisions. They have also confirmed that the ZBL potential represents the repulsive potential of Ni atoms with good accuracy when the repulsive potential energy is higher than a few hundred eV or the interatomic distance is lower than around 0.7 Å.

However, we took a different approach in this study. To see how different functional forms at short interatomic separations affect the sputtering yield, we used a simple repulsive potential function with adjustable parameters that control its functional form. More specifically, we modify an existing EAM potential function by replacing its pair potential ϕ of Eq. (V-1) with

$$\phi^*(r) = [A \exp(-Br) + 1] \phi(r), \quad (\text{V-2})$$

where A and B are numerical parameters. For the potential model P1, we have

$A = 0$. For other potential functions, we set $A = 5,000$ and $B = 9 \text{ \AA}^{-1}$, $12 \text{ \AA}^{-1}$ and $30 \text{ \AA}^{-1}$ and call the EAM function models P2, P3 and P4, respectively, as summarized in Table V-1.

Table V-1 – Parameters used in Eq. (V-2) to modify the interaction potential “Fe-CuNi.eam.alloy” for Ni.

Parameter	Potential			
	P1	P2	P3	P4
A	0	5,000	5,000	5,000
B ($\text{\AA}^{-1}$)	—	9	12	30

The interatomic energies of a pair of Ni atoms as functions of the interatomic distance r are shown for P1, P2, P3, P4 and Q1 in Fig. V-5. It is seen in Fig. V-5a that the interatomic potential energy for P1 is 434 eV at $r = 0$, meaning that a fast-moving atom at a kinetic energy higher than 434 eV would not interact with other still atoms and therefore could easily pass through a thick material consisting of the same type of atoms. This is certainly not realistic but this widely used EAM potential has this functional form simply because it was not meant to be used for such collision phenomena. In this study, we are interested in collision phenomena in the energy range up to a few thousands eV, so the interatomic potential functions must have short-range (e.g., $r < 1 \text{ \AA}$) repulsive interactions in the energy range up to a couple of thousands eV. As seen in Fig. V-5a, a moving atom at a kinetic energy of 1,000 eV can have a hard-sphere-like collision with a still atom, whose collision cross section is given by πa^2 with $a = 0.47 \text{ \AA}$, $0.57 \text{ \AA}$ and $0.72 \text{ \AA}$ if their interatomic potential energy is given by P2, P3 or P4, respectively.

It is also seen in Fig. V-5b, which is a magnification of Fig. V-5a around the potential energy near 0 eV, the interatomic potential functions are essentially the same for all P1 ~ P4 below 5 eV, especially near their energy minimum 0.97 eV at $r = 2.22 \text{ \AA}$. This is because the factor applied to $\phi(r)$ given in Eq. (V-2) is essentially unity around the potential minimum.

For comparison, we also list the model function called Z1, which smoothly connects the potential model P1 for $r > 2.0 \text{ \AA}$ and the ZBL function for $r < 0.3 \text{ \AA}$ in the region $0.3 \text{ \AA} \leq r \leq 2.0 \text{ \AA}$ via the switching function of LAMMPS.

Although not shown here, the Ni ZBL function for all r is hardly distinguishable from the potential model Z1 in Fig. V-5b. As discussed above, the ZBL function is considered to represent the correct repulsive interaction of Ni for an interatomic separation less than about 0.8 Å. The repulsive parts of all other potential models P1, P2, P3, P4 and Q1 are different from that of Z1 and therefore nonphysical. On the other hand, the two-body attractive interactions of the potential models P1, P2, P3, P4 and Z1 are hardly distinguishable, as seen in Fig. V-5b. By definition, the functional forms of P1 and Z1 are identical for $r > 2.0$ Å. Our interest is in clarifying how these different repulsive functions, whether physical or nonphysical, can affect the self-sputtering yield of Ni.

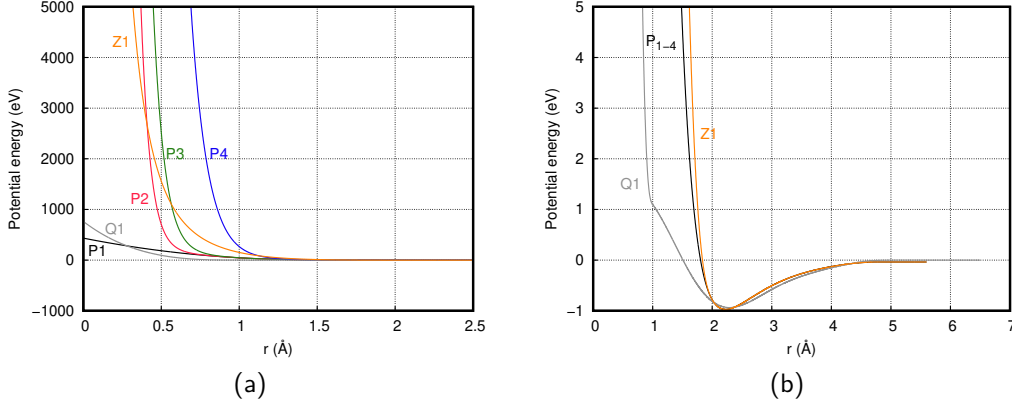


Figure V-5 – Interatomic potential energies between two Ni atoms interacting with the potential functions P1, P2, P3, P4, Q1 and Z1. The potentials P1 and Q1 are the original potential functions given in Figs. V-3 and V-4. The potential energies in a wide energy range are shown in (a) while their form at low-energies are shown in (b). The potential functions of P1 ~ P4 are essentially the same under 5 eV.

V.3 Simulation Results

V.3.1 Mechanical properties

To confirm that the potential models that we use in this study reproduce the same or similar Ni solid, we first evaluated the lattice constant, bulk modulus, Poisson ratio and cohesive energy of the initial substrate shown in Fig. V-1a, using all

the potential models discussed above. Indeed, as discussed earlier, the attractive interactions of Q1, P1 ~ P4 and Z1 shown Fig. V-5b are similar. Therefore, we expect that the mechanical and thermodynamic properties of a material consisting of these atoms are likely to be similar. The evaluation of these quantities was also performed with LAMMPS. The results are summarized in Table V-2 for models P1, P3, Z1, Q1 and M1. The model function M1 is the EAM potential function for Ni proposed by Mishin *et al.*¹⁷¹ smoothly connected to the ZBL potential by the switching function of LAMMPS. It is similar to the DFT-based interatomic potential function for Ni given in Ref. 104. Experimental data are also listed for comparison. Although the data are not shown here, we have confirmed that potential models P2 and P4 also give the same material properties as those of P1 and P3, as expected. It is seen that all the interatomic potential models used in this study represent the Ni material properties with good accuracy.

Table V-2 – Values of some mechanical properties of Ni metal calculated with the potential models P1, P3, Z1, Q1 and M1. Experimental values based on the literature are also listed for comparison.

Model	Lattice constant (Å)	Bulk modulus (GPa)	Poisson ratio	Cohesive energy (eV/atom)
Literature	3.52 ^a	180.4 ^b	0.374 ^b	4.45 ^c
P1	3.520	180.414	0.378	4.450
P3	3.520	180.414	0.378	4.450
Z1	3.520	180.414	0.378	4.450
Q1	3.520	180.997	0.385	4.450
M1	3.519	181.173	0.376	4.449

^a Ref. 172

^b Calculated from data given in Ref. 173

^c Ref. 174

V.3.2 Depth Profiles

The depth profiles of atomic concentrations of Ni are plotted in Fig. V-6. The top and bottom horizontal axes denote the mass and number densities of Ni atoms and the vertical axis denotes the depth in (negative) nm measured from the position of the top surface of the initial substrate. The density as a function of the depth

is calculated as a moving average with a depth interval of 3 Å. The black curves represent the depth profile of Ni atoms that existed in the initial substrate and the blue curve represents the depth profile of Ni atoms that were injected as incident Ni ions. Figure V-6a shows the depth profile of the initial substrate in thermal equilibrium at 300 K, as shown in Fig. V-1a. Figure V-6b shows the Ni substrate after 2,000 Ni ion injection (i.e., an ion dose of $7.1 \times 10^{15} \text{ cm}^{-2}$) with an incident energy of 1,000 eV, as given in Fig. V-1b. The sharply undulating curves seen in Fig. V-6 indicate that the Ni metal is crystalline. The density of the initial substrate of Fig. V-6a over a much larger volume indicates the mass density of this Ni model substrate is 8.9 g cm^{-3} , which agrees with the actual Ni mass density at room temperature. It is seen in Fig. V-6b that the Ni substrate remains crystalline even after ion bombardment and deposited atoms are also located in lattice sites of the crystal. The maximum extent of the penetration depth of 1,000 eV ions is shown to be about 4 nm.

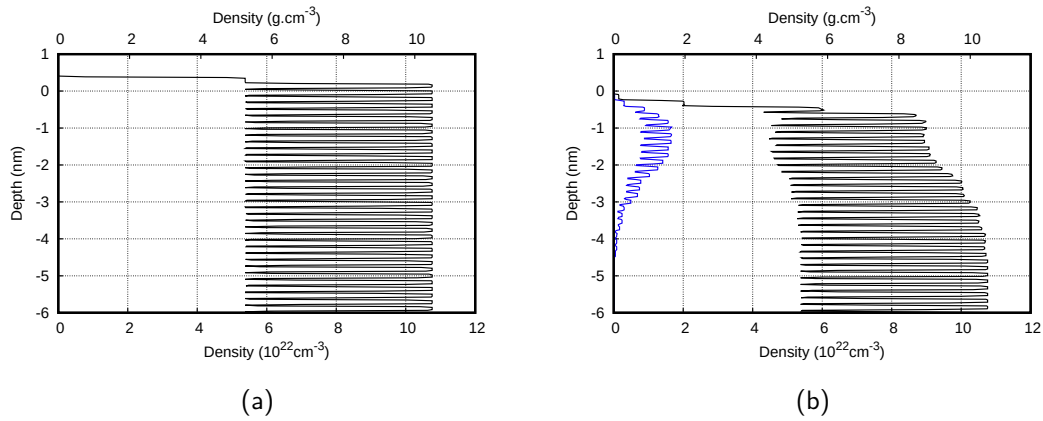


Figure V-6 – Depth profiles of atomic density for (a) the initial Ni substrate and (b) the Ni substrate after 2,000 Ni ion injection (i.e., an ion dose of $7.1 \times 10^{15} \text{ cm}^{-2}$) with an incident energy of 1,000 eV. The density as a function of the depth is calculated as a moving average with a depth interval of 3 Å. The black curves represent the depth profile of Ni atoms that existed in the initial substrate and the blue curve represents the depth profile of Ni atoms that were injected as incident Ni ions. Both substrates are in thermal equilibrium at 300 K.

V.3.3 Evaluation of self-sputtering yield

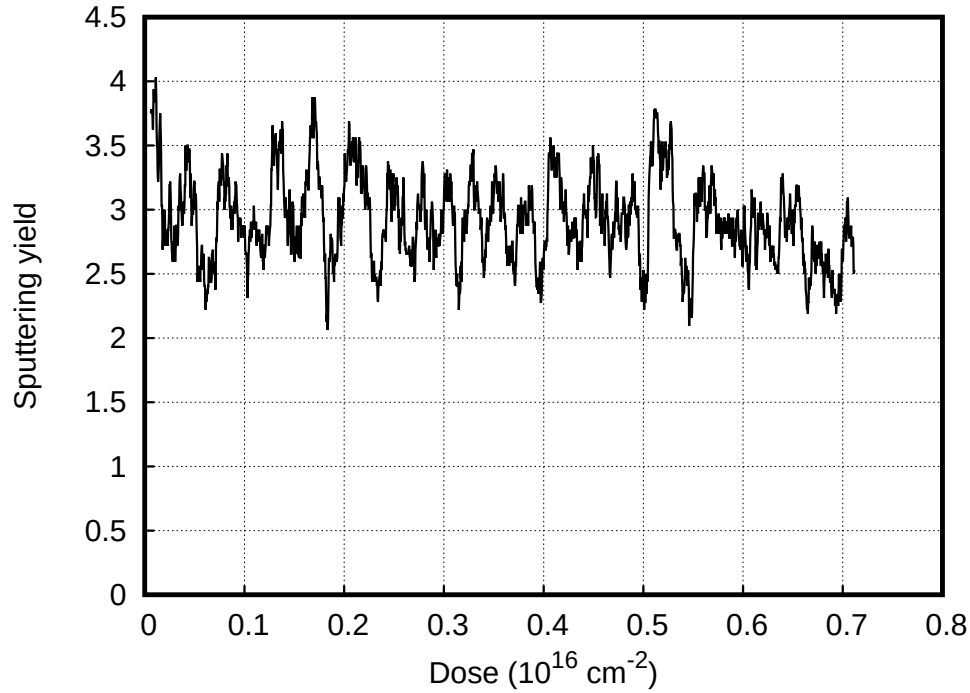


Figure V-7 – Moving average of the instantaneous self-sputtering yields of Ni as a function of the ion dose obtained from MD simulation based on the potential model P3 and the model surface of Fig. V-1a. The ion incident energy is 1.000 eV and the angle of incidence is normal to the surface.

The sputtering yield Y is defined as the average number of atoms that leave the substrate by a single impact of an incident species, i.e.,

$$Y = \frac{N_{\text{sput}}}{N_{\text{in}}} \quad (\text{V-3})$$

with N_{sput} and N_{in} being the total number of atoms that leave (i.e., are sputtered from) the substrate surface and the total number of incident species during the same period. In this study, the incident species is a monoatomic Ni ion, i.e., Ni^+ , and the substrate is a Ni metal. Among the Ni atoms leaving the surface, Ni atoms originating from the surface and those from incident ions cannot be distinguished. In this study, all atoms leaving the system are taken into account in the calculation

of the sputtering yield Y , regardless of their origins. Therefore, a sputtering yield lower than unity, i.e., $Y < 1$, means that the incident ions are deposited on average while a sputtering yield higher than unity, i.e., $Y > 1$, means that the substrate surface is etched. This is consistent with the definition of the self-sputtering yield in earlier studies such as Refs. 57 and 103.

The sputtering yield depends on the surface roughness in general and the surface roughness is caused by ion impact. Therefore, they need to be self-consistently evaluated. In our simulation, the initial surface shown in Fig. V-1a was exposed to incident ions successively without restoring the surface, which causes surface roughness, as shown in Fig. V-1b.

Figure V-7 shows a moving average of the instantaneous self-sputtering yields of Ni as a function of the ion dose obtained from MD simulation. The initial substrate is the one shown in Fig. V-1a with a (100) surface and the interatomic potential model used in this simulation is P3. The ion incident energy is 1,000 eV and the angle of incidence is normal to the initial Ni substrate surface. The moving average is taken over 33 injections (average over the 16 previous, current, and 16 subsequent injections). A single ion injection into the surface area of Fig. V-1 corresponds to an ion dose of $3.6 \times 10^{12} \text{ cm}^{-2}$. It is seen that the sputtering yield fluctuates around its average and becomes nearly independent of the ion dose for large ion doses. To determine the sputtering yield in steady state from the simulation, we typically averaged the instantaneous sputtering yields over an ion dose range from $2 \times 10^{15} \text{ cm}^{-2}$ to the end of the simulation.

The self-sputtering yield Y of Ni at normal incidence thus obtained for various Ni interatomic potential models is summarized as functions of the ion incident energy in Fig. V-8. Here, filled circles are experimental data listed in Ref. 57 and the dashed curve is a semi-empirical fitting curve proposed by Yamamura and Tawara.⁵⁷ In Fig. V-8a, the plus signs, closed squares, open squares, open circles and open triangles represent the self-sputtering yields obtained from MD simulations based on the interatomic potential models P1, P2, P3, P4 and Q1, respectively. Note that the symbols for P1, P3, and P4 at 100 eV and those for P1, P2, and P3 at 500 eV are overlapping. The solid curves and lines connecting the symbols are guides to the eye. It is seen that the self-sputtering yields based on the models P1 ~ P4 tend to be higher than the experimental data whereas those

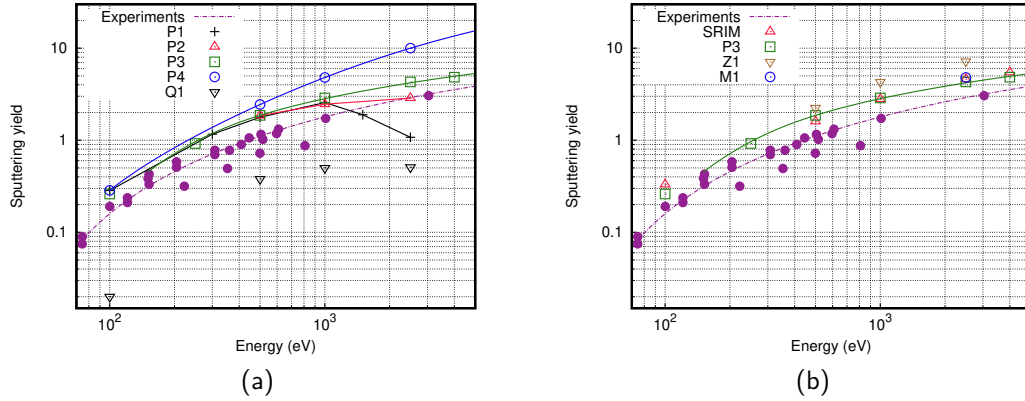


Figure V-8 – Ni self-sputtering yields obtained from MD simulations based on the potential models P1 $\sim$ P4 and Q1 as functions of the ion incident energy, which are compared with experimental data⁵⁷ (filled circles). The angle of ion incident is normal to the surface and the surface orientation assumed for the MD simulations is (100). The dashed curve is a semi-empirical fitting curve proposed by Yamamura and Tawara (Ref. 57). The solid curves and lines connecting the symbols are guides to the eyes.

based on the model Q1 are much lower than the experimental data. Indeed, in the case of Q1, deposition takes place for the entire energy range examined in this study. It is also seen that the short-range repulsive interactions introduced in V-2 strongly affect the self-sputtering yield significantly at high incident energy. As discussed earlier, if the repulsive interactions are weak at high incident energies, the injected ion can pass through the material without much affecting the motion of surface atoms, resulting in low self-sputtering yields. In the energy range examined here, MD simulations based on the interatomic potential model P3 give the self-sputtering yields closest to the experimental data. Furthermore, it is seen that the interatomic potential models P1 and Q1, which have similar two-body attractive interactions at the most stable interatomic distance, as seen in Fig. V-5b, and give similar mechanical properties summarized in Table V-2, lead to very different self-sputtering yields. This indicates that, in addition to the short-range repulsive interaction, the attractive potential model (based on EAM) must be further tuned to give a better prediction of the sputtering yields.

The self-sputtering yields evaluated by the MD simulations are plotted in Fig. V-8a are for the (100) Ni surface of Fig. V-1. Although not plotted here,

the self-sputtering yields evaluated by MD simulations for the (110) surface are found to be nearly the same as those for the (100) surface. On the other hand, the simulation results for (111) surface are found to be higher than those for the (100) and (110) surfaces. [The self-sputtering yields by 1,000 eV ion injections obtained from MD simulations based on the potential model P3 were 2.93, 2.82 and 4.30 for the (100), (110) and (111) surfaces, respectively.] Metspalu *et al.*¹⁰⁵ also reported some variations of Cu self-sputtering yields evaluated by MD simulations over different surface orientations. Hansen *et al.*¹⁰² reported Ni self-sputtering yield between MD simulations and experiments found in this study, therefore, cannot be accounted for by the difference in the surface orientations.

In Fig. V-8b, the self-sputtering yields of Ni evaluated from MD simulations based on the potential models Z1, denoted by inverse triangles, and M1, denoted by empty circles, are given as functions of the ion incident energy. As mentioned earlier, both potential models employ the ZBL potential at shorter interatomic separations, and the potential model M1 is based on the Ni EAM potential function proposed by Mishin *et al.*¹⁷¹ As a reference, the self-sputtering yields of Ni evaluated by SRIM software^{175,176} are also listed, denoted by triangles. In addition, the self-sputtering yields based on the potential model P3, denoted by squares, and experimental data,⁵⁷ denoted by filled circles, both shown in Fig. V-8a are also plotted here for comparison. It should be noted that the SRIM calculation is based on a binary-collision model^{30,86,87} and not an MD simulation. It is seen that the yield values for P3, M1 and SRIM are nearly the same at 2,500 eV. Indeed the yield values obtained from SRIM calculations are in good agreement with those obtained from MD simulations based on the P3 model in the incident energy range examined here. The SRIM gives a slightly higher yield than the MD simulation based on P3 at 100 eV, but it is not clear whether this difference is caused by the lack of multi-body collisions in the SRIM calculation. Although the ZBL potential function is considered to be more physically relevant than the repulsive potential of Eq. (V-2), the yield values based on the Z1 model are shown to be consistently higher than those based on the P3 model and much larger than the experimental data at high ion incident energies.

From Fig. V-8, the self-sputtering yields based on the potential model P3 (and possibly M1) as well as those by SRIM calculations are found to be the

closest to the experimental data but they are also consistently larger than the experimental data by a factor of 2 or so. On the other hand, the yield values based on the potential model Q1 always give the yield values lower than the experimental data over the entire energy range. It suggests that further improvement of the EAM potential functions that are designed to model the material near thermal equilibrium may lead to a better agreement between MD simulation results and experimental observations.

The relative yield for Ni self-sputtering, i.e., the Ni self-sputtering yield normalized at normal incidence, for an ion incident energy of 500 eV is shown in Fig. V-9 as a function of the angle of ion incidence. The angle of incidence is measured from the direction normal to the surface, as usual. The plus signs represent experimental data by Hechtl *et al.*¹⁴⁶ and the solid curve is a guide to the eye. The filled circles represent the relative sputtering yields obtained from MD simulations based on the potential model P3.

It is seen that the sputtering yield increases with the angle of incidence monotonically and peaks around 70°. The simulation results are found to be in reasonable agreement with the experimental data at lower angles. However, as discussed above, the absolute yield values differ by a factor of about 2 between the simulation and experimental data for most angles.

V.4 Conclusions

In this study, we have evaluated the self-sputtering yields of Ni as functions of the ion incident energy and angle, using MD simulations with various interatomic potential models based on the existing EAM potential functions developed for a metallic Ni bulk material. The interatomic potential functions for ions are assumed to be the same as those for charge-neutral atoms for the sake of simplicity. As seen in Fig. V-8a, the Ni self-sputtering yields evaluated by MD simulations based on the original EAM potential P1 of Fig. V-3 are in reasonable agreement with experimental yield values in the energy range below about 1,000 eV. At higher ion incident energy, the short-range repulsive interactions play an important role to determine the correct sputtering yields. As seen in Fig. V-8a, the potential model

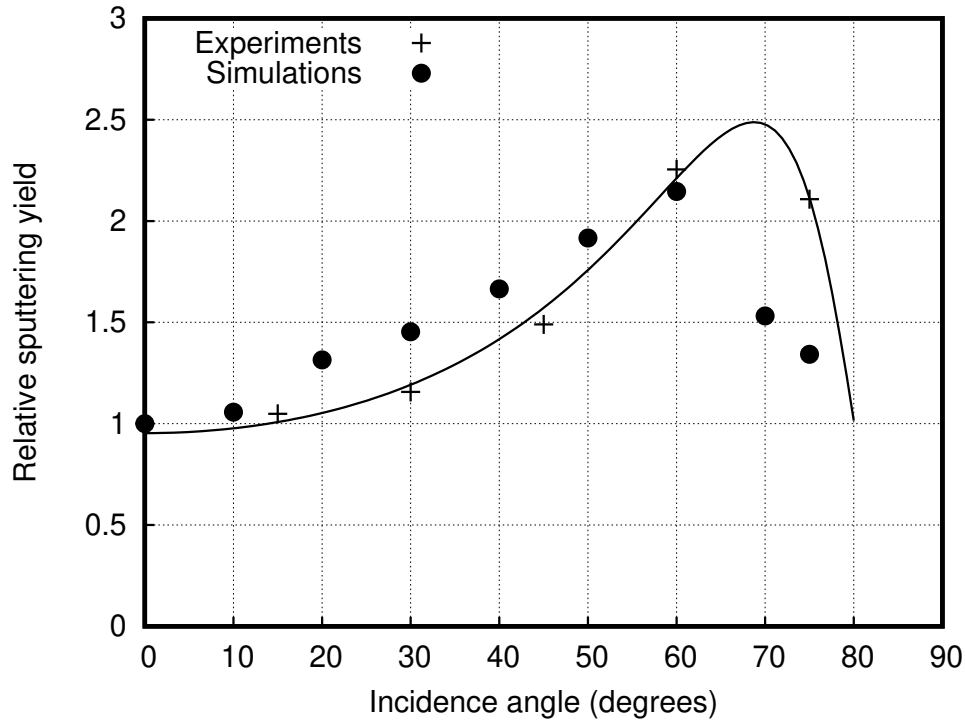


Figure V-9 – Relative yield for Ni self-sputtering, i.e., Ni self-sputtering yield normalized by its value at normal incidence, for an ion incident energy of 500 eV is shown as a function of the angle of ion incidence. The plus signs represent experimental data¹⁴⁶ and the solid curve is a guide to the eye. The filled circles represent the relative sputtering yields obtained from MD simulations based on the potential model P3.

P3, which has the same functional form as that of P1 except at short interatomic separations, gives the sputtering yield closest to the experimental values in the energy range that we examined. On the other hand, the sputtering yield based on the potential model Q1 of Fig. V-4, which is also designed for bulk Ni metal, are found to be significantly lower than the experimental values.

These facts indicate that the use of existing interatomic potential functions designed for bulk materials may not be adequate, or may even fail, to predict sputtering yields. This is not surprising because the bulk properties of a material are determined by the interactions of atoms around their equilibrium positions whereas sputtering phenomena are more closely related to bond breaking, i.e., atomic interactions away from their equilibrium positions, as well as atomic colli-

sions, i.e., repulsive atomic interactions at close interatomic separation. An earlier study¹⁰⁷ has also shown based on analyses of a large number of sputtering data that the values of various sputtering properties are strongly correlated with a relatively small number of physical parameters such as the atomic mass of incident ions and atomic mass, number density, and heat of formation of the surface material. Given the fact that the heat of formation is strongly correlated with the bond energy of the surface atoms and the atomic collision processes in the surface material depend on the atomic mass and atomic radius (which is correlated with the atomic mass and number density of the material) for a given ion incident energy, the results of Ref. 107 also seem to imply that the balance between the repulsive and attractive interactions strongly affects the sputtering phenomena.

The potential model P3, which is based on the nonphysical repulsive function of Eq. (V-2), gives the self-sputtering yields close to the corresponding experimental values. They are even closer to the experimental data than the potential model Z1 based on the ZBL function at short interatomic separation. Although both P3 and Z1 have essentially the same attractive EAM potential functions, the evaluation of their sputtering yields presented in this study by no means indicates that repulsive potential of Eq. (V-2) is better than the ZBL potential. The selection of the model function P3 may be just fortuitous; the nonphysical repulsive potential of Eq. (V-2) may happen to be balanced well with the approximate representation of Ni bonds by the EAM potential of V-3, reproducing sputtering yields close to the experimental data.

We also observed that the sputtering yields based on the potential model Q1 were much lower, even at the low-energy range where the repulsive interaction was less important. This result suggests that an attractive potential model (possibly formulated as an EAM model) that is more accurate than both P1 and Q1, combined with an appropriate short-range repulsive potential function, may provide self-sputtering yields even closer to the experimental data.

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sputtering yields even closer to the experimental data.

In this sense, it should not be construed the promotion of the model function of Eq. (V-2) over the ZBL function as the short-range repulsive potential model. On the contrary, the ZBL function should be used for a short-range repulsive potential function as it is based on a physical interpretation of short-range atomic interactions. The model function of Eq. (V-2) was introduced in this study only to show how a continuously changing repulsive potential function could affect the self-sputtering yield values.

It is also seen in Fig. V-8b that the SRIM calculations give Ni self-sputtering yields that are similarly close to the experimental data in the energy range considered in this study. Because an SRIM calculation is computationally much less time-consuming than the corresponding MD simulation, it seems to negate the need to perform MD simulations to estimate the sputtering yields. However, it is not clear *a priori* that SRIM or any binary-collision model^{30,86,87} provides the correct sputtering yield values⁷² for low-energy ion injections. At low incident ion energy, where multi-body collisions are considered to play important roles, MD simulations are likely to offer a more self-consistent description of the sputtering phenomena, including dynamical phenomena such as collision cascades, energy deposition and dissipation, and phonon propagation in the material during a sputtering process. In this sense, MD simulation is still worth studying as a potential theoretical tool to evaluate sputtering yields and analyse other physical phenomena.

The angular dependence of the sputtering yield was found to be in reasonable agreement between the numerical simulations and experiments for the incident ion energy (500 eV) examined here. It is seen in Eq. (V-9) that the agreement is better for small incident angles. When the angle of incidence is large, recoil atoms near the surface tend to move in lateral directions (i.e., directions parallel to the surface) or even in the direction away from the surface toward free space as they are pushed forward by the collision cascade initiated by the incident ion impact. Such atoms have a higher chance of breaking away from the surface. This is in contrast with the case of normal ion incidence, where most atoms are pushed inward, i.e., toward the bulk of the material first and less likely to leave the surface. This is the reason that the sputtering yield increases with an increasing

angle of incidence, up to a certain angle. When the angle of incidence is too large and glancing, the incident ion is more likely to be reflected upon impact and the momentum and energy transfer from the incident ion to the material surface is limited, resulting in a small sputtering yield. Because energetic ions impacting on the surface at a glancing angle may give some momenta to the near-surface atoms in the direction tangential to the surface, whether such surface atoms break away from the surface or not depends sensitively on the interactions of near-surface atoms reacting to shear stress that moves the atoms toward the bond-breaking positions. The interatomic potential functions constructed for bulk materials in their thermodynamic equilibrium are typically not designed to handle such atomic motions. It is surmised this is the reason that the prediction of the peak position of an angular-dependent sputtering yield by MD simulation tends to be subject to large errors.

The electronic stopping power^{45,177–179} is known to have no effect on the motion of incident ions and recoil atoms in this energy range. Therefore, to further improve the MD simulation capability to evaluate the sputtering yield correctly, the improvement of interatomic potential functions should be the first step to be taken. The development of more accurate interatomic potential functions for Ni (and possibly other metals) that can reproduce both mechanical and thermodynamic properties and sputtering properties with high accuracy is the subject of a future study.

Molecular dynamics simulation of Si trench etching with SiO₂ hard masks

Typical sizes of semiconductor devices in large-scale integrated (LSI) circuits have continued to shrink for the last several decades and now been approaching atomic scales. Plasma etching has been the key technology for the formation of nanometer-scale structures on material surfaces and therefore contributed significantly to the miniaturization of semiconductor devices. For this reason, plasma etching processes are widely used in semiconductor device manufacturing.^{6–10,13,180}

Plasma etching is a removal process of atoms from the material surface by the influxes of chemically reactive species and/or energetic ions emitted from a plasma. It is also called reactive ion etching (RIE) because the surface etching reactions are typically due to the synergetic effects of surface chemical reactions with incident reactive species and collision cascades caused by ion impact.^{11,12} As opposed to RIE, ion beam etching (IBE) refers to the etching by ion beam injection only. In both RIE and IBE, the sputtering yield is defined as the average number of removed atoms of specific species for a single ion impact. In the case of RIE, the sputtering yield also depends on the radical fluxes.

When the sizes of structures formed on a material surface are of the order of nanometers, the randomness of ion impacts during the etching and the mechanical strength of atomic-scale surface structures can significantly affect the final shapes

of etched structures. There have been many efforts to predict the etched profiles based on the macroscopic models,^{53–55,118,119,181–185} where the evolution of the surface profiles is determined by the local “velocities” of the surface, i.e., the local etch rates. An implied premise of such profile models is that the surface is always smooth macroscopically and there is a mechanism such as surface diffusion that would smooth out atomic-scale surface roughness and thus prevent any instability that could allow an atomic surface roughness to grow to a macroscopic one. In etching and deposition processes for the formation of nanometer-scale structures, such a premise is typically violated.

The goal of this study is to demonstrate how surfaces and underlying subsurface regions of atomic-scale structures can evolve when they are subject to IBE and RIE. The method that we employed is classical molecular dynamics (MD) simulation, which allows us to visualize the changes in material structures during etching processes. The validity of the application of our MD simulation to the materials that we examined in this study was partially corroborated by existing experimental data.

The main concern of this study is the following three issues; the individuality of incident ions and radicals, transient effects of etching, and local mechanical strengths of the materials. Even if nanometer-scale mask surface structures are exposed to uniform fluxes of incident ions and radicals during the etching process, the way individual ions impact the surface randomly can affect the patterns of surface roughness at the atomic level. Sputtered atoms and clusters of atoms can be redeposited on the facing surfaces and nonuniform deposition of sputtered species can also induce additional surface roughness. Such atomic-level surface roughness always existed in etching processes but was not considered important when the device structures were much larger, e.g., of submicron scale. However, it could even affect the device performance if the device structure is of a nanometer scale.

When a pristine material is exposed to a uniform and constant reactive ion and radical fluxes, its surface chemical compositions, crystallinity, and morphology may continue to change until the etching process reaches steady state. In this initial and transient phase of etching, for example, the surface may swell as it incorporates incident chemical species before the surface height decreases due to

the etching reactions. For a composite material such as silicon dioxide (SiO_2), specific atomic species may be preferentially sputtered initially, leading to the surface chemical compositions that are significantly different from those of the bulk material. In the case of SiO_2 , oxygen (O) atoms are sputtered more preferentially than silicon Si atoms. For an etching process of nanometer-scale structures, which typically requires a relatively small ion dose (i.e., fluence), a significant part of the etching process may fall into this transient initial phase and, accordingly, the etched structures can be significantly affected by these transient effects.

The local mechanical strengths of nanometer-scale structures of a material can be significantly different from that of the bulk of the same material. This is because the surface-to-volume ratio of a nanometer-structure is typically large. The mechanical strength of a subsurface region is considered to be lower than that of the bulk because of the deficiency of atoms supporting its structure. In this chapter, we use the term “mechanical strength” rather vaguely, referring to the level of resistance of a nanometer-scale material against possible deformation. A quantitative definition of the local mechanical strength will be deferred to a future study. In general, nanometer-scale structures are more prone to deformation and erosion even by low-energy ion bombardment, and therefore considered as “mechanically weak”, than larger-scale structures.

In this study, we demonstrate trench etching of a crystalline silicon (Si) surface covered by a SiO_2 mask with a 5 nm wide gap by Cl^+ IBE and RIE with chlorine plasmas. The trench structure examined in this study is motivated by that of shallow trench isolation.¹⁸² The model material consists of atoms used in the MD simulation. In the etching process simulations, the individuality of incident ions and radicals, transient effects of etching, and local mechanical strengths of the material are all incorporated self-consistently.

Etching of Si by Cl^+ ions has been studied widely and its sputtering yield has been obtained as a function of incident ion energy.^{60,64,126,186–188} Experimentally obtained sputtering yields of SiO_2 may be found in Ref. 189. MD simulations have been extensively performed to evaluate the sputtering yields and/or surface modifications of Si and SiO_2 by Cl^+ ions and Cl radicals.^{37,96,160,190–194} The sputtering yields of Si and SiO_2 by Cl^+ ions obtained from MD simulations are in general in reasonable agreement with the experimental observations.

The remainder of this chapter is organized as follows: in the Sect. VI.1, we discuss the simulation method of this study, and in Sect. VI.2, we present MD simulation results for flat surfaces and trench structures. Discussion of the simulation results and the summary of the study are given in Sect. VI.3. Sect. VI.4 presents the conclusion.

VI.1 Simulation conditions

VI.1.1 Model surfaces

In this study, we performed MD simulations to investigate etching processes of Si and SiO₂ by chlorine (Cl) ions and radicals. In MD simulation, Newton's equation of motion is solved numerically for each atom with given interatomic force models. The interatomic potential functions used in this study were essentially the same as the Stillinger-Weber potential functions presented in Ref. 37.

First Si and SiO₂ flat surface models were examined as etched materials. The Si flat surface model was made of Si atoms arranged in a diamond crystalline structure with a lattice constant of $a_{\text{Si}} = 5.43 \text{ \AA}$ and its top surface orientation was (100). It had a rectangular shape, having lengths of 3.26 nm, 3.26 nm and 2.17 nm in the x , y (horizontal) and z (vertical) directions, respectively, and consisted of 1,152 Si atoms. Periodic boundary conditions were imposed in the horizontal directions and therefore the model represented an infinitely wide Si slab.

Similarly the SiO₂ flat surface model was made of Si and O atoms in a β -cristobalite structure with a lattice constant of $a_{\text{SiO}_2} = 6.98 \text{ \AA}$ and its top surface orientation (in an idealized model of β -cristobalite structure) was (100). It has a rectangular shape, having lengths of 4.19 nm, 4.19 nm and 2.79 nm in the x , y and z directions, respectively, and consisted of 1,152 Si atoms and 2,304 O atoms, totalling 3,467 atoms. As in the Si flat surface model, periodic boundary conditions were imposed in the horizontal directions and therefore the model represented an infinitely wide SiO₂ slab. Both material models were thermalized at 300 K. Figure VI-1 shows these models.

Second, we also examined a two-layer trench-structure model material representing a (100) crystalline Si surface covered with a SiO₂ hard mask, as shown in

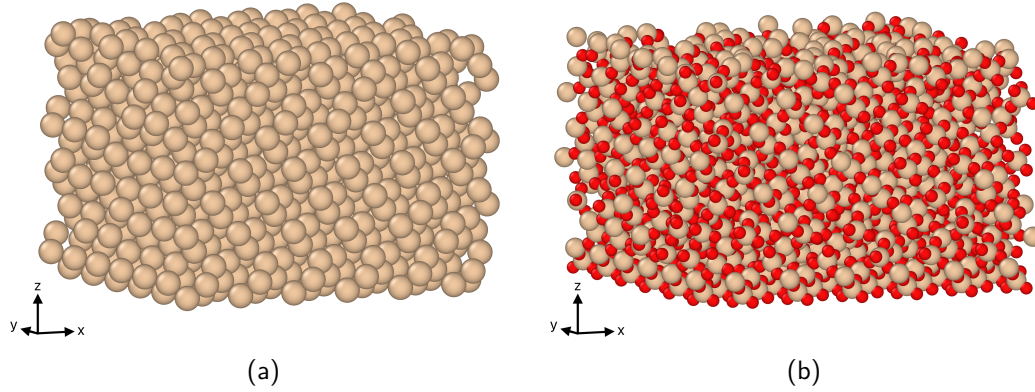


Figure VI-1 – Three-dimensional (3D) representations of the (a) Si and (b) SiO₂ flat surface models in thermal equilibrium at 300 K, used in this study. Beige and red spheres represent Si and O atoms. The model sizes are 3.26 nm, 3.26 nm and 2.17 nm for Si and 4.19 nm, 4.19 nm and 2.79 nm for SiO₂ in the x , y and z directions.

Fig. VI-2(a). It was 14.66 nm $\times$ 4.89 nm wide in the horizontal directions (x and y) and 14.62 nm long in the vertical direction (z). The lower layer was a 4.85 nm-thick crystalline Si substrate with a (100) top surface and the upper layer of the material was a 9.77 nm-thick crystalline SiO₂ mask. A 5 nm-wide trench was cut through the SiO₂ mask in the y direction to expose the Si surface to incident ions and radicals. In total, the model was composed of 27,302 Si atoms and 21,952 O atoms, totalling 49,254 atoms. Among the 27,302 Si atoms, 16,524 belonged to the Si substrate and 10,778 to the SiO₂ mask. As in the flat surface models, periodic boundary conditions were imposed in the horizontal (x and y) directions.

In real Si etching processes, SiO₂ used as a hard mask is amorphous, not crystalline. In this study, we use a crystalline SiO₂ mask for the sake of simplicity. The sputtering yield or etching rate of high-density amorphous SiO₂ (whose density is similar to that of crystalline SiO₂) is considered to be similar to that of crystalline SiO₂. This is because, even in etching of crystalline SiO₂, its top surface is constantly modified and converted to amorphous due to the ion-impact induced surface damage.

The averaged number of Si and O atoms per unit depth over a unit horizontal area is plotted as functions of the depth in Fig. VI-2(b). For the bottom Si layer,

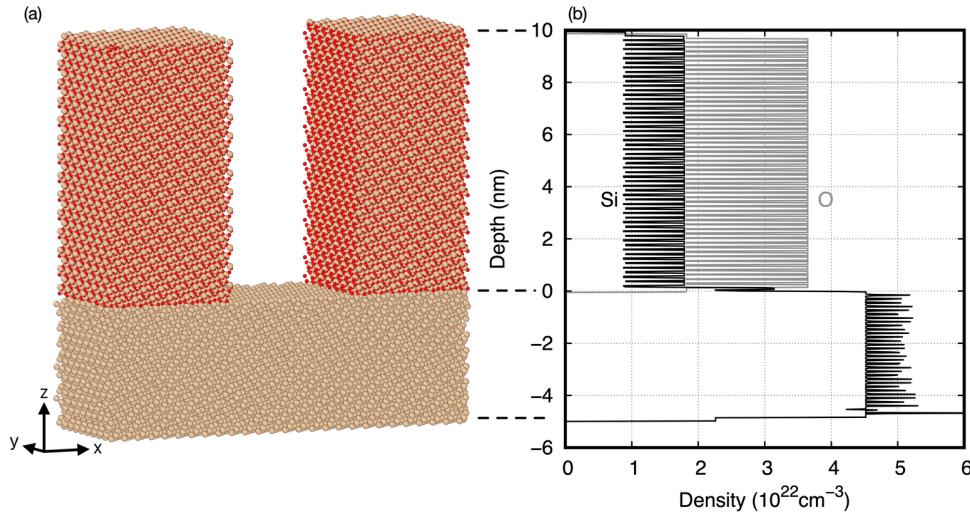


Figure VI-2 – (a) 3D representation of the trench-structure model material in thermal equilibrium at 300 K, used in this study. Beige and red spheres represent Si and O atoms. (b) Depth profiles of the numbers of Si (black curve) and O (grey curve) per unit depth over a unit horizontal surface area. The value corresponds to the local Si number density in the lower Si layer. For the upper SiO₂ mask layer, it represents 2/3 of the local Si or O number density because of the presence of the trench gap. For the sake of brevity, the horizontal axis is labeled as “Density” in (b). The origin of the depth $z = 0$ is taken at the interface between the Si and SiO₂ layers.

the value corresponds to the number density of Si atoms at each depth. On the other hand, the value represents two-thirds of the Si or O number density of SiO₂ on the mask layer because of the presence of the trench gap. This averaged number of each atomic species was evaluated as a running average of the corresponding value with a depth interval of 3 Å. The sharply undulating curves indicate that the materials are crystalline. The origin of the depth $z = 0$ of Fig. VI-2(b) is set at the position of the interface between the upper SiO₂ mask layer and the lower Si layer, such that a negative depth $z < 0$ corresponds to the Si layer whereas a positive depth $z > 0$ corresponds to the SiO₂ mask of this model. The horizontal axis is labeled as “Density” for brevity.

VI.1.2 Ion/radical injection cycles

Etching simulations by incident ions and radicals were performed in a way similar to earlier MD simulation studies.^{97–100,106,134,160,195,196} The model material was placed at the bottom of the simulation box which has the same horizontal dimensions as those of the material. As mentioned earlier, periodic boundary conditions were imposed in the horizontal directions. The top boundary of the simulation box was set sufficiently high such that the simulation box could enclose all injected and sputtered atoms during the simulation until they were removed from the simulation box. To prevent the material from going downward, the bottommost few layers of the material were fixed in position during the simulation.

In the etching simulation, the material's top surface was exposed to incident Cl^+ ions and possibly Cl radicals in a cyclical way. (In typical Cl plasma etching, Cl_2^+ ions may also be generated, but we focus on the etching effects caused by Cl^+ ions in this study. We do not consider Ar^+ ions, either, which may arise from Ar gas used in a process gas mixture for Cl-based plasma etching.) In an odd-number injection cycle, Cl radicals were emitted from the gas phase toward the material surface with a given incident energy and randomly selected (downward) incident angles. The number of Cl radicals emitted in a single cycle is denoted by N_{Rad} . The kinetic energy of radicals was typically set low, comparable to thermal energy in general.

In an even-number injection cycle, Cl^+ ions were injected into the material surface with a given incident energy at normal incidence, i.e., along the z -axis. The number of Cl^+ ions emitted in a single cycle is denoted by N_{Ion} . For the sake of simplicity, no charge effect of incident Cl^+ ions was considered and therefore a Cl^+ ion was modeled as a charge-neutral Cl atom. The only difference between ions and radicals was that an ion typically had a much higher initial kinetic energy than a radical species. Accordingly, the effect of surface charges accumulated by positive ion impacts is not considered here, either. The accumulated surface charge may retard the incident ion energy and reduced the ion flux by deflecting some incident ions. However, the simulation results depend on the actual ion impact energy and ion dose (but not the ion flux, i.e., the ion dose per unit time). Therefore, with an appropriate interpretation of the simulation results, the surface charge-up effect

does not alter the conclusions of this study.

The ratio of the number of injected Cl radicals to that of Cl⁺ ions per single cycle is denoted by $\Gamma = N_{\text{Rad}}/N_{\text{Ion}}$, which represents the ratio of the radical to ion fluxes. In the case $\Gamma = 0$, no Cl radical is injected, meaning that the process is an IBE with Cl⁺ ions. When $\Gamma \neq 0$, we call the process an RIE.

Cyclic injections of ions and radicals were used for the convenience of numerical simulation. In reality, of course, ions and radicals are emitted randomly. Under typical process plasma conditions, the ion and radicals fluxes are low enough such that no two ionic or radical species would simultaneously impact the same location of the surface. Therefore, each ion and radical impact is considered as an independent event and the impact order does not affect the etching results.

The initial positions of the emitted Cl radicals or Cl⁺ ions were selected randomly on a horizontal plane sufficiently high above the top surface of the model material. In actual simulations, however, all emitted ions and radical species high above the material surface were moved along their straight paths (i.e., orbits) to the proximity of the material surface just outside their atomic interaction range with surface atoms before each injection cycle of the simulation started. In this way, all incident ions and radicals were emitted just above the material surface with their given initial velocities and the computational time required for their gas-phase motion can be saved significantly. For simulation results shown in this article, the kinetic energies for ions and radical species were set at 100 eV and 0.1 eV, respectively. The ion kinetic energy was set to 100 eV to keep a reasonable etch rate with respect to the calculation time although it is understood that a better selectivity could be achieved with a lower ion kinetic energy. The radical kinetic energy was set slightly higher than its thermal energy at 300 K to further reduce the time required for gas-phase radicals to reach the material surface without much affecting their interaction with the surface.

As etching proceeded and the thickness of the model material was no longer thick enough, some energetic atoms could reach the bottommost layer during the simulation. When it happened, we abandoned this particular ion/radical injection cycle, added several new layers of the material to the bottom from the lower side to make the material thicker and restarted the current ion/radical injection cycle from its beginning.

We denote the time in each injection cycle by t . In each injection cycle, at $t = 0$, ions or radicals were emitted toward the material surface from the gas phase, as discussed above. The material was set to be in thermal equilibrium at $T = 300$ K at $t = 0$. For the first 500 fs of this cycle, MD simulation was performed under the constant energy (NVE) conditions to update the position and velocity of all atoms. From $t = 500$ fs, a Langevin cooling²² was applied for 1.4 ps, followed by a Brendsen cooling²¹ for 0.1 ps to thermalize the system at $T = 300$ K. The cycle ends at $t = 2.0$ ps. At the end of the injection cycle, all atoms not belonging to the surface material (i.e., all atoms in the gas phase) were removed from the simulation box. After this, a new injection cycle was started unless the number of ion/radical injection cycles reached the predetermined value.

The cooling process above is a numerical simulation technique to bring the system expeditiously to thermal equilibrium. In reality, with typical ion fluxes used in plasma processing, the typical time interval for which two consecutive ions hit a particular nanometer-scale area is several orders of magnitude larger than 2 ps. This is the reason that all gas-phase atoms in the simulation box were removed at the end of the injection cycle, under the assumption that they would move away sufficiently far from the material surface by the time the next ion or radical species emitted from the beam or plasma system arrived at the surface.

In our MD simulation, the cooling operation was typically applied only to the atoms belonging to the surface material and those in the gas phase were allowed to move without slowing down. This allowed sputtered atoms traveling in the

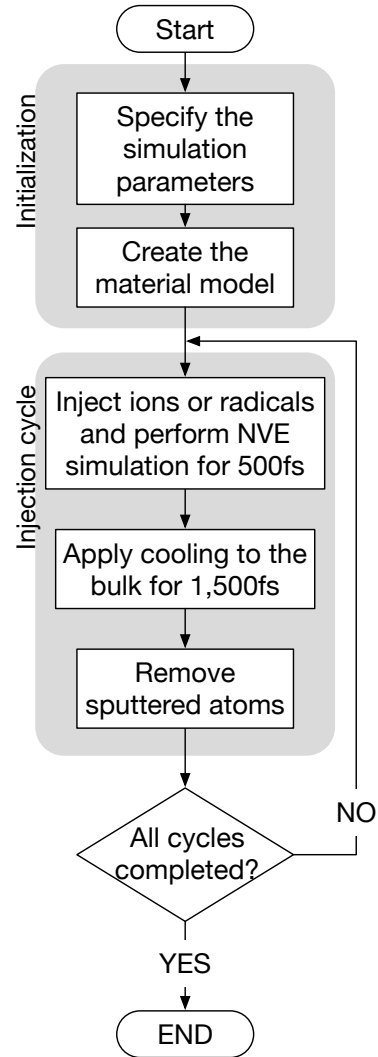


Figure VI-3 – Flow chart of the MD simulation used in this study.

trench gap to reach the facing surface and to interact with the surface atoms there for redeposition or reflection. Slow sputtered/desorbed atoms in the trench space might not reach the facing surface during the 2 ps injection cycle and, if so, they were removed from the simulation box at the end of the cycle. Therefore we might have underestimated the surface redeposition in our MD simulation. We tried MD simulations with various injection-cycle periods and concluded that the 2 ps injection cycle is reasonable and practical and the possible underestimation of surface redeposition did not affect the etched surface morphology much under the etching conditions discussed in this study. The flow chart of the simulation is presented in Fig. VI-3.

VI.2 Results

VI.2.1 Etching of flat surfaces

We first studied Cl⁺ IBE and Cl based RIE of Si and SiO₂ flat surfaces. The model materials used in this study were shown in Fig. VI-1. In IBE simulation, each model material was exposed to a single Cl⁺ ion per cycle ($N_{\text{Ion}} = 1$) with an incident ion energy of 100 eV. In RIE, each material was exposed to 10 Cl radicals in each odd-number cycle ($N_{\text{Rad}} = 10$) with a kinetic energy of 0.1 eV and a single Cl⁺ ion in each even-number cycle ($N_{\text{Ion}} = 1$) with an incident ion energy of 100 eV. As discussed earlier, the initial direction of each Cl radical was set randomly and that of each Cl⁺ ions was in the negative z direction. The initial positions of simultaneously emitted 10 Cl in each cycle were selected sufficiently away from each other such that no two Cl atoms would collide or form a Cl₂ molecule before reaching the surface.

Figure VI-4 shows the instantaneous sputtering yields for Si and O atoms as functions of the ion dose for IBE and RIE, obtained from MD simulations. The instantaneous sputtering yield is a running average of the number of Si or O atoms removed from the surface per ion impact over an ion dose interval of $3.11 \times 10^{14} \text{ cm}^{-2}$ for Si or $1.88 \times 10^{14} \text{ cm}^{-2}$ for SiO₂ (i.e., over 33 ion injections into each model surface). In each case, a total of 2,000 Cl⁺ ions were injected into the substrate model, which corresponds to an ion dose of $1.88 \times 10^{16} \text{ cm}^{-2}$ for the

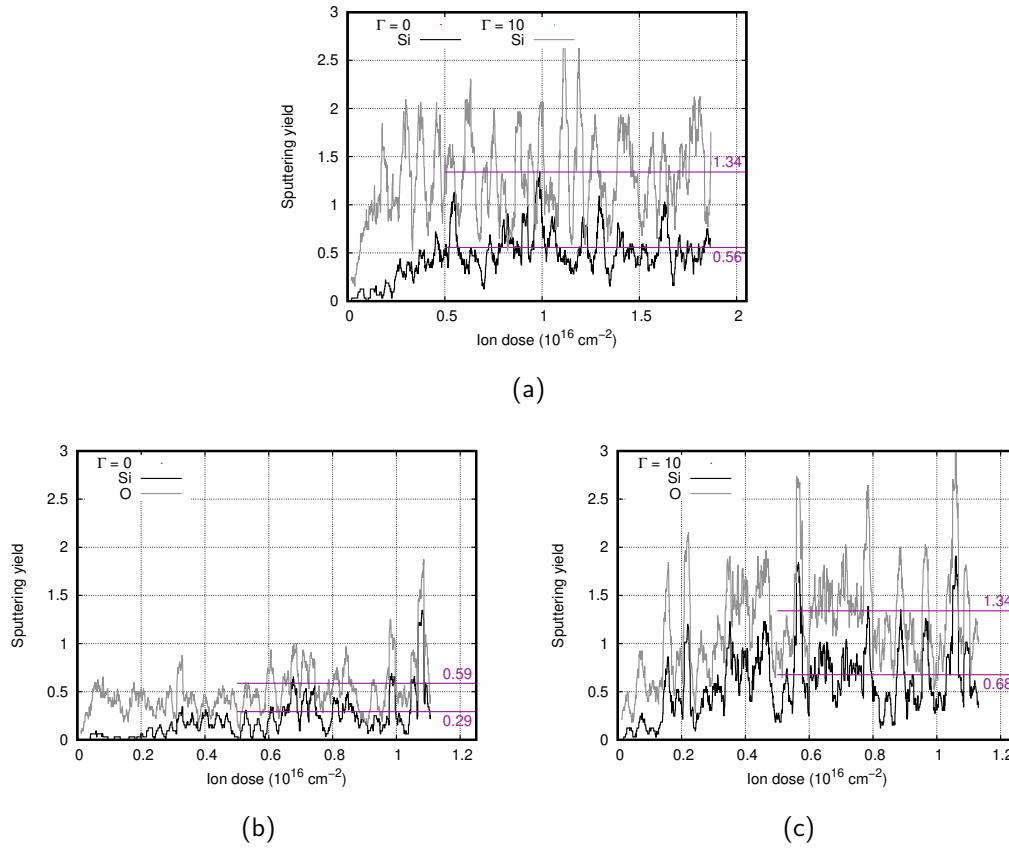


Figure VI-4 – Instantaneous sputtering yields of flat (a) Si and (b)(c) SiO₂ surfaces by Cl⁺ IBE ($\Gamma = 0$) and chlorine-based RIE ($\Gamma = 10$) as functions of the ion dose. Γ is the flux ratio of Cl radicals to Cl⁺ ions. The sputtering yield in steady state is the yield averaged over the ion dose indicated by the purple line, i.e., from an ion dose of $0.5 \times 10^{16} \text{ cm}^{-2}$ to the end of the simulation. The obtained sputtering yield values in steady state are indicated in the graphs. The incident ion energy was 100 eV and the angle of ion incidence is normal to the surface.

Si surface and $1.14 \times 10^{16} \text{ cm}^{-2}$ for the SiO₂ surface. In RIE, no Cl radical dose is counted in the horizontal axes of Fig. VI-4 but Si and O atoms removed in all injection cycles (including the radical injection cycles) were also counted in the evaluation of the RIE sputtering yields.

The sputtering yield in steady state was evaluated as the yield averaged from an ion dose of $0.5 \times 10^{16} \text{ cm}^{-2}$ to the end of the simulation. The sputtering yields of Si atoms for Si and SiO₂ surfaces by 100 eV Cl⁺ IBE were found to be

0.56 and 0.29, which are in reasonable agreement with the existing experimental data.^{60,64,126,186–189}

It is seen that, in both IBE and RIE, the sputtering yield of Si is higher than that of SiO₂ by a factor of around 2. Similarly, for each material, the sputtering yield of RIE ($\Gamma = 10$) is higher than that of IBE by a factor of around 2. It indicates that the presence of low-energy Cl radicals significantly enhances the sputtering yields. In actual plasma etching, Γ can be as high as 100 or more, so the sputtering yield enhancement by RIE can also be significantly higher.

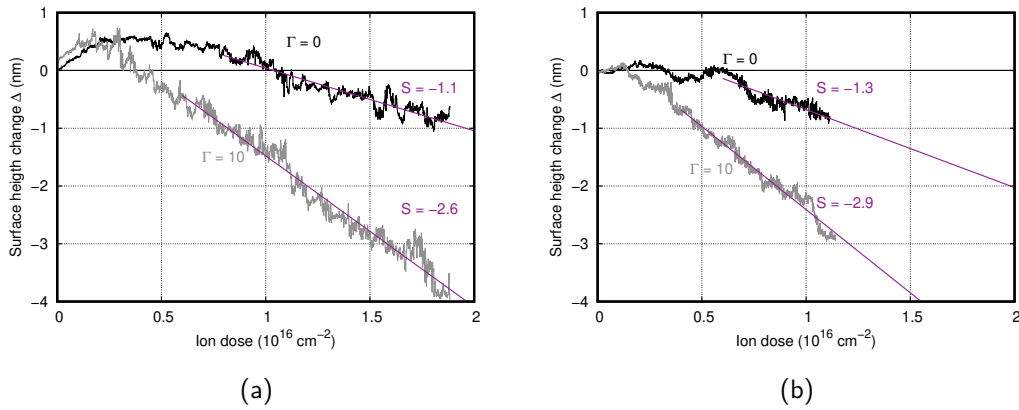


Figure VI-5 – Surface height change Δ of a (a) Si or (b) SiO₂ flat surface as a function of the ion dose. The slope S in steady state is indicated by a purple line for each curve and its value is given in units of 10^{-24} cm^3 . The etching conditions are the same as those given in Fig. VI-4.

Although the sputtering yield of SiO₂ is lower than that of Si, it does not mean that the rate of erosion or etch rate of SiO₂ is equally lower than that of Si. This is because the number density of Si atoms in SiO₂ is also lower than that of Si. We also evaluated the change in the surface height during the IBE and RIE processes obtained from the same MD simulations. The exact position of the top surface height is defined as the z coordinate at which the atomic number density of the material is 10^{22} cm^{-3} .

Figure VI-5 shows the change in surface height Δ of the (a) Si and (b) SiO₂ model materials during IBE (black curves) and RIE (grey curves) with $\Gamma = 10$ as functions of the ion dose. As in Fig. VI-4, the horizontal axes represent the ion

dose only. The change of the surface height per ion dose, i.e., the slope or gradient of Δ in Fig. VI-5 is now denoted by S . In steady state, the relation

$$S = \frac{Y}{n}$$

holds with Y and n being the sputtering yield and the atomic number density of the material. The value of S represents the average volume removed from the surface by a single ion impact.

It is seen in Fig. VI-5a that the Si surface height increased or the Si surface swelled initially before the height eventually went down as the etching proceeded. This is because the surface incorporated some of the incident Cl atoms. For Cl^+ IBE, this initial swelling continued up to an ion dose of around $1.0 \times 10^{16} \text{ cm}^{-2}$. For Cl-based RIE with $\Gamma = 10$, the surface went down much faster and the initial swelling continued only up to $0.4 \times 10^{16} \text{ cm}^{-2}$. As seen in Fig. VI-5b, the SiO_2 surface hardly swelled during the etching process. This is because, as seen in Fig. VI-4 (b) and (c), O atoms were preferentially sputtered off initially, which decreased the surface region volume of the SiO_2 material.

After the material initial swelling, the surface height steadily decreased as the etching proceeded. In steady state, the Si surface height decreased at a rate of $S = -1.1 \times 10^{-24} \text{ cm}^3$ for IBE and $S = -2.6 \times 10^{-24} \text{ cm}^3$ for RIE with $\Gamma = 10$. For SiO_2 , these rates are $S = -1.3 \times 10^{-24} \text{ cm}^3$ for IBE and $S = -2.9 \times 10^{-24} \text{ cm}^3$ for RIE with $\Gamma = 10$. It is observed that both Si and SiO_2 showed similar values of S for each set of etching conditions, indicating the rates of erosion for Si and SiO_2 were similar in the etching processes examine in this study. This indicates that the SiO_2 mask needs to be at least as thick as the planned etched depth of Si.

VI.2.2 Trench etching

In this subsection, IBE and RIE of trench structures are discussed. The model material to be etched is shown in Fig. VI-2(a). Because its surface area is much larger than those of Si and SiO_2 flat surface models, in the IBE simulation, the material was exposed to 10 Cl^+ ion per cycle ($N_{\text{Ion}} = 10$) to increase the simulation efficiency. Each Cl^+ ion was injected in the negative z direction with a kinetic energy of 100 eV. The initial positions of simultaneously emitted 10 Cl^+ ions in

each cycle were selected sufficiently away from each other such that no two ions would hit nearby surface locations. Similarly, in the RIE simulation with $\Gamma = 10$, the material was exposed to 80 Cl radicals in each odd-number cycle ($N_{\text{Rad}}=80$) and 8 Cl⁺ ions in each even-number cycle ($N_{\text{Ion}} = 8$). Each Cl⁺ ion was injected in the negative z direction with a kinetic energy of 100 eV. As in the case for flat surface RIE simulations discussed earlier, the incident direction of each Cl radical species was selected randomly and its initial kinetic energy was set at 0.1 eV.

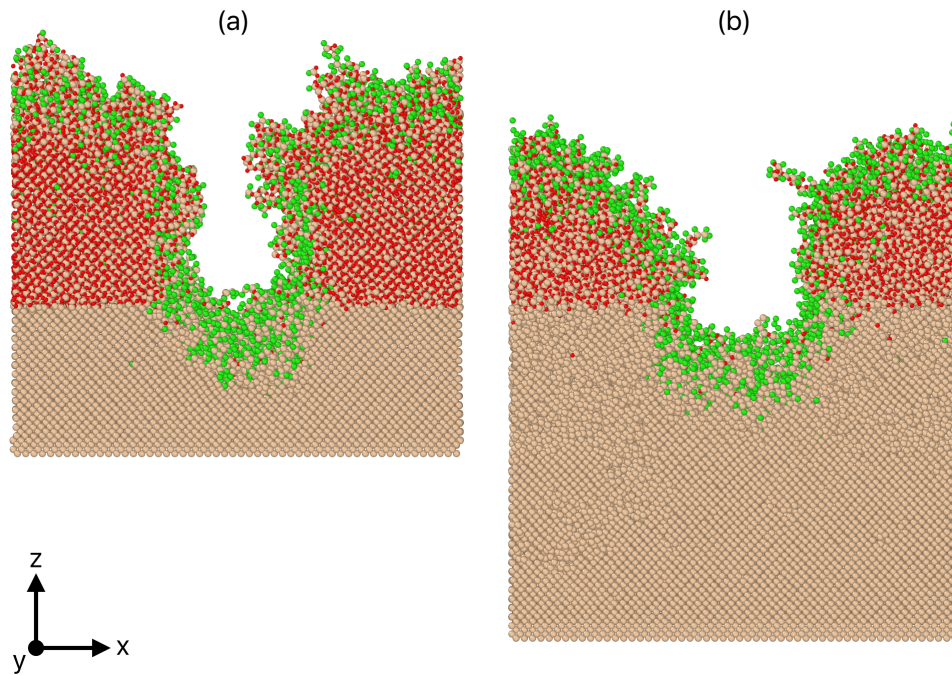


Figure VI-6 – Representation of the front views of the trench-structure model materials of Fig. VI-2 after 100 eV Cl⁺ ion injections with an ion dose of $1.65 \times 10^{16} \text{ cm}^{-2}$ (12,000 Cl⁺ ion injections) for (a) IBE and (b) RIE with $\Gamma = 10$, obtained from MD simulations. The angle of ion incidence was normal to the initial flat surface. Beige, red and green spheres represent Si, O and Cl atoms, respectively. Periodic boundaries were applied in the horizontal directions. The material was in thermal equilibrium at 300 K during the process. In (b), the bottom Si layers were automatically added during the simulation such that the plasma-surface interactions would not be affected by the finite depth of the model material.

Figure VI-6 shows the etched trench-structure model materials of Fig. VI-2 after 100 eV Cl⁺ ion injection with an ion dose of $1.65 \times 10^{16} \text{ cm}^{-2}$ (12,000 Cl⁺ ion

injections) for (a) IBE and (b) RIE with $\Gamma = 10$, obtained from MD simulations. As we discussed earlier, because the etch rates of Si and SiO₂ for RIE are larger than those for IBE, the erosion and tapering of the SiO₂ mask proceeded more for RIE than IBE. Accordingly, incident Cl⁺ ions and knocked-on Si and O atoms affected deeper regions of the Si layer in RIE. Therefore, in (b), the bottom Si layers were automatically added during the simulation such that the plasma-surface interactions would not be affected by the finite depth of the model material.

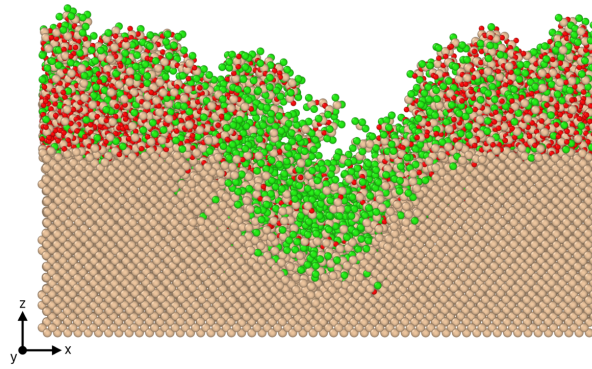


Figure VI-7 – The etched trench-structure material of Fig. VI-6(a) at a higher ion dose of $4.18 \times 10^{16} \text{ cm}^{-2}$ (30,000 Cl⁺ ions injections) for IBE, obtained from MD simulations. It is seen that the mask collapsed and the trench etch stopped.

It is seen that the etched profiles are much different between IBE and RIE. For IBE, the Si layer was only slightly etched with a tapered profile, indicating that the etching proceeded more at the center of the trench than near the sidewalls because of the protruding SiO₂ mask. For RIE, the trench structure of the etched Si layer is easily visible with a relatively flat bottom surface, indicating that the trench mask pattern was better transferred to the etched Si layer for RIE than IBE.

The higher etch rate of RIE seems to remove mechanically weak structures of the mask more efficiently, preventing the mask collapse. For IBE, because of its relatively low etch rate, the mask tends to deform more before it is removed by etching. Our study also showed that, with a higher ion dose of IBE, the SiO mask eventually collapsed and prevented the trench etching of the Si layer, as shown in Fig. VI-7. On the other hand, our preliminary study showed that, with a higher

ion dose in RIE, the mask was further eroded before a deep trench was formed in the Si layer.

It should also be noted that, even in RIE, the thickness of the removed SiO₂ mask is much larger than the etched depth of Si. If the etch rates of Si and SiO₂ were the same, this would not occur. This occurred because, owing to the transient effects discussed above, while the etched Si surface swelled, the erosion of SiO₂ continued. As discussed earlier, for an etching process of nanometer-scale structures, a significant part of the etching process may fall into this transient initial phase and, therefore, the etched profiles can be significantly influenced by these effects.

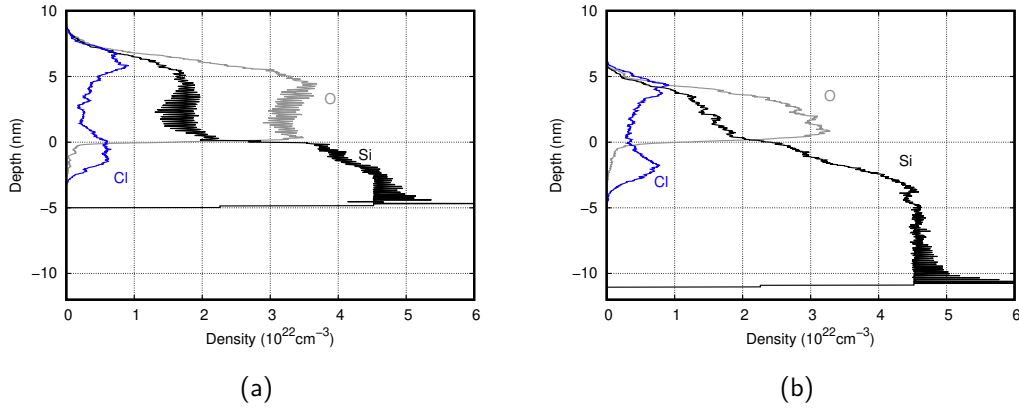


Figure VI-8 – Depth profiles of the numbers of Si (black curve), O (grey curve) and Cl (blue curve) per unit depth over a unit horizontal surface area for (a) IBE and (b) RIE with $\Gamma = 10$ after 100 eV Cl⁺ ion injections with an ion dose of $1.67 \times 10^{16} \text{ cm}^{-2}$, corresponding to the etched trench-structure model materials of Fig. VI-6. The initial depth profiles are given in Fig. VI-2(b).

Figure VI-8 shows the depth profiles of the numbers of Si (black curve), O (grey curve) and Cl (blue curve) per unit depth over a unit horizontal surface area for (a) IBE and (b) RIE with $\Gamma = 10$, corresponding to the etched trench-structure model materials of Fig. VI-6. The initial depth profiles are given in Fig. VI-2(b). It is seen in Fig. VI-8 that the mask material was lost more and the lower Si layer was etched more in RIE than in IBE. The slightly peaked profiles of the numbers of Si and O atoms at around $z = 4 \sim 5$ nm in Fig. VI-8a indicate that the Cl⁺ ion bombardment deformed the mask and caused the protrusions of the mask sidewalls

in IBE. It is also observed that the ratio of the Si to O densities near the top of the SiO₂ mask is close to unity in both IBE and RIE. It results from the preferential sputtering of O atoms from SiO₂, which makes the top surface of a SiO₂ mask more Si rich than its bulk.

VI.2.3 Etched surface profiles

The sidewall surfaces of the etched trench structures shown in Fig. VI-6 may be better seen in Fig. VI-9, where the model materials of Fig. VI-6 (a) and (b) were cut in half along the y -axis at $x = 7.3$ nm. To visualize the averaged surface structures better, we also constructed coarse-grained surfaces, using the following algorithm.

We first define cubic 3D grids covering the entire material and having a spacing of 1 Å in each direction. At each grid point, the material density was computed as $n = N/V$, where N is the number of atoms within a distance $R = 3$ Å from the grid point and V is the volume of the sphere of radius R , given by $V = 4\pi R^3/3$. As we defined the surface height for Fig. VI-5, we define a grid point being occupied by a material as that with $n > 10^{22} \text{ cm}^{-3}$.

We then define enveloping surfaces that characterize the trench sidewalls in the following manner. Starting from the midplane located at $x = 7.3$ nm that cut the etched trench structure at the center of the trench, as seen in Fig. VI-9, we move along the x -axis toward the material edges and find the first two sets of grid points where the material exists. These two sets of points define the left and right sidewall surface profiles. Connecting all such grid points over the entire y and z coordinates, we obtain coarse-grained enveloping surfaces formed along the x -axis as shown in Fig. VI-10.

Although the roughness of sidewalls seems similar between IBE and RIE, it is seen in (a) that part of the sidewalls, especially the right sidewall near the top surface, protrudes more toward the trench center in IBE. The etched Si surface at the bottom of the trench is wider and flatter for RIE (b) than for IBE (a).

We also construct coarse-grained enveloping surfaces along the z -axis to show the averaged structures of the etched top surfaces of SiO₂ and Si. Starting from a sufficiently high xy plane, we search for the highest grid point of the material along

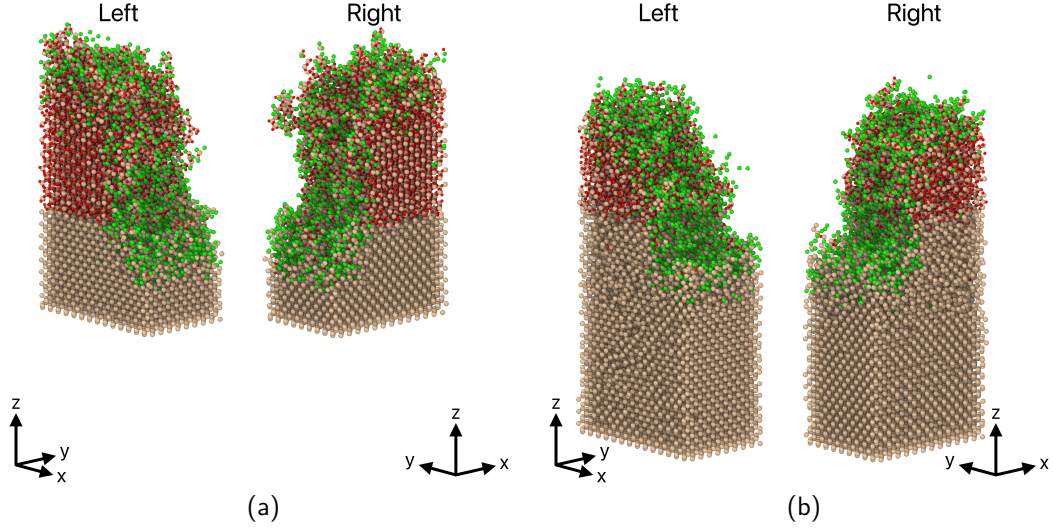


Figure VI-9 – Three-dimensional representation of the sidewalls of etched trench-structure model materials of Fig. VI-6 for (a) IBE and (b) RIE with $\Gamma = 10$. The material models were cut in half along the y -axis at $x = 7.3 \text{ nm}$.

the z -axis. Connecting all such grid points over the entire x and y coordinates, we obtained the coarse-grained enveloping surfaces, as shown in Fig. VI-11. It is seen that, in IBE, the etched bottom surface is narrower in this representation than in reality, owing to the protruding structures of the sidewalls. On the other hand, the trench pattern of the original mask was better transferred to the Si layer in RIE.

VI.3 Discussion and Summary

In this study, we examined trench etching of Si surfaces covered with SiO₂ hard masks by Cl⁺ IBE and Cl-based RIE, using MD simulation. The simulation results shown in this article are those by 100 eV Cl⁺ ion injections with an angle of incidence being normal to the horizontal surface. For RIE, in addition to the Cl⁺ ion beam, Cl radicals were simultaneously emitted from the gas phase with kinetic energy close to their thermal energy with randomly selected angles of incidence. The flux ratio of Cl radicals to Cl⁺ ions in the RIE simulations presented in this

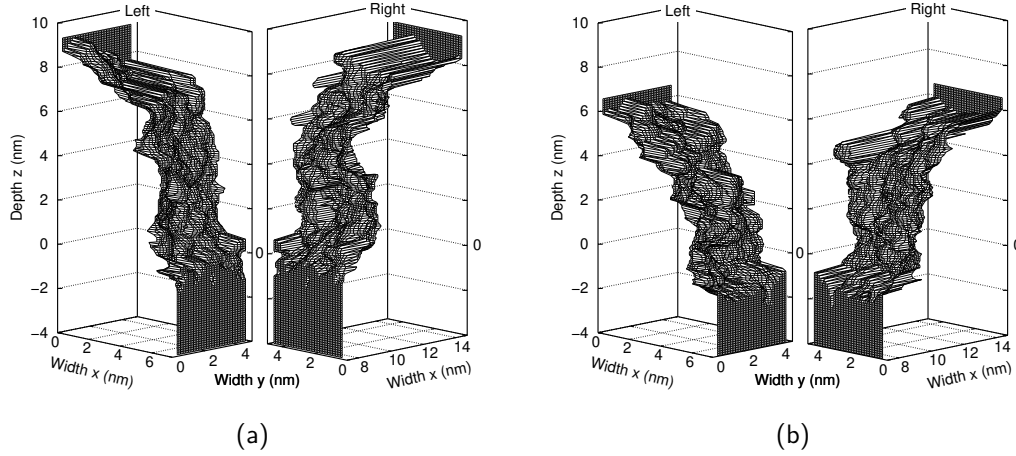


Figure VI-10 – Coarse-grained enveloping surfaces formed along the x -axis of the etched trench-structure model materials of Fig. VI-6 for (a) IBE and (b) RIE with $\Gamma = 10$, representing the averaged surface roughness of the sidewalls shown in Fig. VI-9.

article was $\Gamma = 10$.

The sputtering yields of Si and SiO₂ obtained from MD simulations were found to be consistent with experimental observations. The sputtering yield of Si was around twice larger than that of SiO₂ for both IBE and RIE. The exposure of the material surface to Cl radicals alongside with Cl⁺ ion injections enhanced the sputtering yield approximately by a factor of 2 for both Si and SiO₂. However, the number density of Si atoms in SiO₂ is much lower than that in solid Si, the etch rates of Si and SiO₂ were found to be similar. This indicates that the SiO₂ mask needs to be at least as thick as the planned etched depth of Si under these etching conditions.

Our MD simulations found that etched profiles were significantly different between IBE and RIE with $\Gamma = 10$. For IBE, etching was more due to physical sputtering than chemical etching and the etched Si surface was tapered with the centerline of the trench being more deeply etched than the edges in contact with the mask sidewalls. The weakness of the mask structure also showed up as more severely deformed sidewalls in IBE, which tend to prevent incident ions from reaching the edges of the trench bottom. On the other hand, in RIE, both mask and Si layer were etched faster. The width of the etched Si trench was closer to the

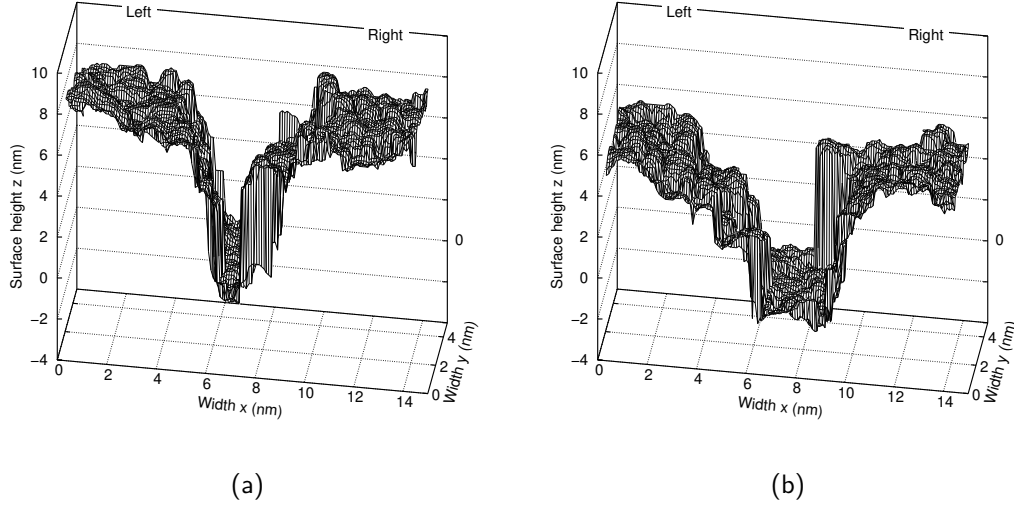


Figure VI-11 – Coarse-grained enveloping surfaces formed along the z -axis of the etched trench-structure model materials of Fig. VI-6 for (a) IBE and (b) RIE with $\Gamma = 10$, representing the averaged surface roughness of the top and bottom surfaces shown in Fig. VI-9. It is seen that the erosion and tapering of the mask is more significant for RIE (b) than for IBE (a) because of the higher etch rates of RIE.

original width of the mask opening, exhibiting better pattern transfer fidelity in RIE. The trench bottom was also found to be flatter in RIE. The higher etch rate of the RIE seemed to prevent the formation of highly protruding structures of the mask because the RIE tended to remove deformed rough surfaces more quickly than the IBE. The less deformation of the mask sidewalls allowed more uniform exposure of the trench bottom to the incident ions.

Although the initial profiles of the mask and the underneath Si layer were perfectly symmetric around the centerline of the trench and the ion and radical fluxes were also completely uniform, the etched structures, especially those of mask sidewalls, significantly differed on the left and right sides. This reflects the fact the etched profiles of nanometer-scale structures can be easily affected by the individuality of incident ions and radicals emitted randomly. The way the atomic-scale roughness is created strongly depends on how randomly emitted ions and radicals interact with the surface atoms and the size of such roughness is comparable with the sizes of the desired etched structures. Therefore, in IBE or RIE of nanometer-

scale structures, the formation of line width roughness seems unavoidable. Well designed atomic layer etching (ALE) may reduce such roughness.^{195,197–203}

It should also be noted that, even in RIE, the thickness of the removed SiO₂ mask is much larger than the etched depth of Si. If the etch rates of Si and SiO₂ were the same, this would not occur. This occurred because, owing to the transient effects discussed above, while the etched Si surface swelled, the erosion of SiO₂ continued. As discussed earlier, for an etching process of nanometer-scale structures, a significant part of the etching process may fall into this transient initial phase and, therefore, the etched profiles can be significantly influenced by the transient effects.

The local mechanical strength of etched materials can also significantly affect the etched profiles of nanometer-scale structures, as we just discussed above. A nanometer-scale thin material layer near the surface is typically weaker in mechanical strength than the bulk due to the shortage of surrounding supporting atomic structures. Furthermore, its chemical composition can be easily modified by etchant ions and radicals during the etching process, which typically reduces its mechanical strength further. Our MD simulations demonstrated that, in IBE, the bulged mask sidewalls resulting from the ion bombardment blocked part of the ion flux toward the bottom of the trench. The simulations also showed that efficient chemical etching due to the presence of Cl radicals contributed significantly to the formation of smoother mask walls in RIE, which resulted in a better pattern transfer than in IBE.

VI.4 Conclusions

This study has demonstrated the etched profiles of nanometer-scale structures are strongly affected by the individuality of incident ions and radicals, transient effects of etching such as the initial swelling of an etched surface, and insufficient mechanical strengths of the ion-damaged surfaces. Although the incident ion and radical fluxes are uniform in space, the etched surface cannot be uniform at the atomic level due to these effects. RIE and IBE based on simple Cl chemistry with 100 eV Cl⁺ ions resulted in significant erosion of SiO₂ mask and rough etched

surfaces of Si. For better etched-profile control of nanometer-scale structures, an etching process with lower ion energy and possibly more elaborate surface chemistry is required. For example, addition of oxygen to the incident species may allow the sidewall passivation and replenish some oxygen lost from the mask. A further study is needed to confirm such effects quantitatively.

Conclusions

In this thesis, molecular dynamics (MD) simulations have been performed to investigate the sputtering mechanism of different systems to give a better understanding of the physical sputtering mechanism and unveil the dependency of the physical sputtering yield on physical parameters, such as the incident ion energy or mass.

The Chap. II presents the computational background of the numerical simulations performed in this study. The first part of the chapter focuses on describing the background of MD simulations, which consists in computing the system dynamics by solving the Newton's equation of motion for each atom. The second part focuses on the interatomic potential function V , a key element of MD simulations which directly define the system dynamics. The four potential functions used in this study are presented: the Lennard-Jones (LJ), the screen-Coulomb, the Stillinger-Weber and the embedded atom method (EAM) potential functions. The last part of the chapter focused on some material properties. At the end of the chapter, several material properties used during the study are presented.

In Chap. III, the physical self-sputtering yield of a LJ solid, i.e., a material made of atoms interacting through a Lennard-Jones (LJ) potential function, is studied. All interactions between atoms are represented using a Lennard-Jones (LJ) potential function and the incident particles are identical to the material atoms. It is shown that the physical self-sputtering yield presents a universal curve which only depends on the incident angle and on the normalized incident

energy $\mathcal{E}$, which is defined as the ratio of the incident ion energy to the parameter ε of the LJ potential function. It therefore represents the relative energy of the incident ion to the bond strength of the material. The self-sputtering yield was evaluated over a wide range of the normalized energy $\mathcal{E}$ and the obtained universal curve of the physical self-sputtering was compared to experimental self-sputtering yields of iron (Fe), nickel (Ni) and copper (Cu) and showed a good agreement at low incident energies. At higher incident energies, however, the LJ self-sputtering yields significantly differs from experimental yields. This divergence is because the repulsive interactions of the LJ potential do not represent those of actual atoms at short distances. To obtain a better agreement for high incident energies, the repulsive part of the LJ potential was modified to make it less repulsive. Self-sputtering yields using this modified LJ potential functions showed a good agreement over the studied energy range.

The study is extended in Chap. IV to the case where incident particles and material atoms are of different species. Material atoms are interacting through a LJ potential function, whereas the interactions with incident particles are represented with a repulsive LJ potential function. The sputtering yield Y then becomes a function of the normalized incident energy $\mathcal{E}$, defined as the ratio of the incident energy to the LJ parameter ε , the ratio of the atom masses μ and the relative interaction range ρ , which is a function of the LJ parameters ε and σ . The physical sputtering yield Y was evaluated for a range of values of $\mathcal{E}$, μ and ε . Over this range of values, the physical sputtering yield varies by order of magnitudes. The parameters μ and ρ were evaluated from the cohesive energy E_C and the nearest-neighbour distance d for several materials. It was found that they have a strong correlation, being linearly related, and vary with a narrow range with $0.3 < \mu < 3$ and $0.8 < \rho < 1.2$. In this range of values, the physical sputtering yield Y are similar, which is also observed in experimental physical sputtering yields.

In Chap. V, the physical self-sputtering of specific material, nickel (Ni), is studied using a popular potential function for metallic systems, the embedded atom method (EAM) potential function. The physical sputtering yield of a crystalline Ni material was calculated for a range of incident energies up to a few thousands eV for several potential models. These potential models are based on existing EAM potential functions for Ni, where the potential at low interatomic distances

was modified. The comparison with experimental physical self-sputtering yield for Ni shows that, although the different potential models can accurately reproduce mechanical properties of a bulk Ni material, they may not be able to accurately reproduce the sputtered properties of the material. This is especially true for large incident energies, where the used potential model, i.e., the interaction cross-section at low interatomic distances, was found to have a significant effect on the physical self-sputtering yield.

In Chap. VI, trench etching of Si surfaces covered by SiO₂ hard masks was studied for Cl⁺ ion beam etching (IBE) and Cl-based reactive ion etching (RIE). In IBE, 100 eV Cl⁺ ions were injected at normal incidence. In RIE, alongside with Cl⁺ ions, Cl radicals were simultaneously injected with a kinetic energy close to their thermal energy with random incidence angles, with a flux ratio of Cl radicals to Cl⁺ ions in RIE of 10. The etching of Si and SiO₂ surfaces was first studied for both IBE and RIE. It was found that, for both IBE and RIE, the sputtering yield of Si was around twice larger than that of SiO₂. For both Si and SiO₂, the exposure of the surface to Cl radicals alongside to Cl⁺ ions (RIE) was found to enhance the sputtering yield by a factor of 2 compared to when the material is only exposed to Cl⁺ ions (IBE). However, the etch rate of Si and SiO₂ were found to be similar due to the much lower Si density in SiO₂ than in solid Si. The etched profiles were significantly different between IBE and RIE. For IBE, the etched profile was tapered with the centerline of the trench more deeply etched than the edges in contact with the sidewalls. The mask was also more severely deformed, which tends to prevent incident ions from reaching the edges of the trench bottom. For RIE, on the other hand, the etched profile was found flatter and its width was closer to the original width of the mask trench, exhibiting better pattern transfer fidelity. The mask was less deformed, allowing a more uniform exposure of the trench bottom to incident ions.

In the following, three appendices are available to the reader.

In Append. A, the derivation of the velocity-Verlet algorithm from the Verlet algorithm is given. Although these two algorithms are mathematically equivalent, they are numerically quite different.

The Append. B shows the calculation of the lattice constant l_a and the cohesive energy E_C for a LJ solid, i.e., for a material made of atoms interacting through a

LJ potential function. In this case, they can be evaluated from the parameters ε and σ of the LJ potential function. The lattice constant l_a is a linear function of σ whereas the cohesive energy is a linear function of ε .

The Append. C discusses the extension of the LJ system studied in Chap. IV to a full LJ system. The repulsive LJ potential function used to represent the interactions with the incident particle is replaced by a full LJ potential function. In this case, the dynamic depends on additional parameters which correspond to the ratio of the LJ parameter ε .

Velocity-Verlet algorithm

The velocity-Verlet algorithm is a mathematically equivalent expression of the Verlet algorithm which has the advantage to be self-starting and to avoid rounding errors for the calculation of the velocity.

The Verlet algorithm is given by (Eq. (II-7)):

$$x_{n+1} = 2x_n - x_{n-1} + a_n \Delta t^2 \quad (\text{A-1a})$$

$$v_n = \frac{x_{n+1} - x_{n-1}}{2\Delta t} \quad (\text{A-1b})$$

First, we use Eq. (A-1b) to express x_{n-1} as $x_{n-1} = x_{n+1} - 2v_n \Delta t$ and we inject it into Eq. (A-1a) to obtain x_{n+1} :

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} a_n \Delta t^2 \quad (\text{A-2})$$

We then use Eq. (A-1a) to express x_{n+2} and Eq. (A-1b) to express v_{n+1} :

$$x_{n+2} = 2x_{n+1} - x_n + a_{n+1} \Delta t^2 \quad (\text{A-3a})$$

$$v_{n+1} = \frac{x_{n+2} - x_n}{2\Delta t} \quad (\text{A-3b})$$

By substituting Eq. (A-3a) into Eq. (A-3b), we obtain:

$$v_{n+1} = \frac{x_{n+1} - x_n}{\Delta t} + \frac{a_{n+1} \Delta t}{2} \quad (\text{A-4})$$

Finally, by substituting Eq. (A-2) into Eq. (A-4), we obtain:

$$v_{n+1} = v_n + \frac{1}{2}a_n\Delta t + \frac{1}{2}a_{n+1}\Delta t \quad (\text{A-5})$$

The velocity-Verlet algorithm is formed by Eqs. (A-2) and (A-5):

$$x_{n+1} = x_n + v_n\Delta t + \frac{1}{2}a_n\Delta t^2 \quad (\text{A-6a})$$

$$v_{n+1} = v_n + \frac{1}{2}(a_n + a_{n+1})\Delta t \quad (\text{A-6b})$$

LJ crystal — Lattice constant and cohesive energy

For a LJ crystal, i.e., for a material made of atoms interacting through a LJ potential function, the nearest-neighbour distance R_0 , the lattice constant l_a and the cohesive energy E_C can be evaluated from the two LJ parameters σ and ε .

The LJ potential function between two atoms is given as:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (\text{B-1})$$

Here, r denotes the interatomic distance between the two interacting atoms. σ and ε are the two parameters of the LJ potential function.

B.1 Nearest-neighbour distance and lattice constant

To calculate the nearest-neighbour distance R_0 and the lattice constant l_a , we consider the total energy E_T of a system of N atoms, obtained by taking the summation over all the neighbours j :

$$E_T = 4\varepsilon \frac{N}{2} \left[\sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^6 \right] \quad (\text{B-2})$$

Here, $p_{ij}R$ denotes the distance between the i -th and j -th atoms expressed in terms of the nearest-neighbour distance R . The factor $1/2$ comes from the fact that bonds are counted twice.

The values of the summations have been calculated.²⁰⁴ For the fcc structure, we have:

$$\sum_j p_{ij}^{-12} = 12.1318 \quad \sum_j p_{ij}^{-6} = 14.4539 \quad (\text{B-3})$$

Considering E_T (Eq. (B-2)) as the total energy of the crystal, the nearest-neighbour distance at equilibrium R_0 is such that the total energy E_T is minimum with respect to variations of the nearest-neighbour distance R :

$$\frac{dE_T}{dR} = 0 = -2N\varepsilon \left[145.58 \frac{\sigma^{12}}{R^{13}} - 86.72 \frac{\sigma^6}{R^7} \right] \quad (\text{B-4})$$

We then obtain the relation between the nearest-neighbour distance at equilibrium R_0 and the LJ parameter σ :

$$R_0 \simeq 1.09\sigma \quad (\text{B-5})$$

In a fcc crystal, it is known that the nearest-neighbour distance is the distance between the atom located in the middle of a face and an atom located at one of the vertices of the face, i.e., along the diagonal of a face of the cube. Therefore, the relation between the nearest-neighbour distance R_0 and the lattice constant l_a is given by:

$$l_a = \sqrt{2}R_0 \quad (\text{B-6})$$

Using Eq. (B-5), we obtain the relation between the lattice constant l_a and the LJ parameter σ :

$$l_a \simeq 1.54\sigma \quad (\text{B-7})$$

B.2 Cohesive energy

The cohesive energy is the energy needed to separate the material constituents into independent neutral atoms at ground state. Typically, the cohesive energy is given as an energy per atom to have a quantity independent of the system size, i.e., an intensive quantity. The cohesive energy E_C is given as the total energy E_T at equilibrium divided by the number of atoms N .

By substituting Eqs. (B-3) and (B-5) into Eq. (B-2), we obtain:

$$E_C = \frac{E_T(R_0)}{N} = \frac{2N\varepsilon}{N} \left[12.13 \left(\frac{1}{1.09} \right)^{12} - 14.45 \left(\frac{1}{1.09} \right)^6 \right] \quad (\text{B-8})$$

The relation between the cohesive energy E_C and the LJ parameter ε is given by:

$$E_C \simeq -8.56\varepsilon \quad (\text{B-9})$$

Extension of sputtering of LJ solid

In Chap. IV, the sputtering of a LJ solid was studied by considering that interactions with incident particles are represented by a repulsive LJ potential function. Here, we look at the changes induced by considering that all interactions are represented by a full LJ potential function.

C.1 Extension to full LJ systems

Instead of the repulsive LJ potentials of Eqs. (IV-1b) and (IV-1c), full LJ potential functions are employed. The potential functions are then expressed as:

$$\begin{aligned} V_{\alpha\alpha}(r) &= 4\varepsilon_{\alpha\alpha} \left[\left(\frac{\sigma_{\alpha\alpha}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\alpha}}{r} \right)^6 \right] \\ V_{\alpha\beta}(r) &= 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] \\ V_{\beta\beta}(r) &= 4\varepsilon_{\beta\beta} \left[\left(\frac{\sigma_{\beta\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\beta\beta}}{r} \right)^6 \right] \end{aligned}$$

The normalized equations of motion corresponding to Eq. (IV-3) become:

$$\begin{aligned} \frac{d\bar{\mathbf{v}}_i}{d\tau} = & - \sum_{j \in \alpha} \frac{\partial}{\partial \xi_i} \left(\frac{1}{\xi_{ij}^{12}} - \frac{1}{\xi_{ij}^6} \right) \\ & - \sum_{j \in \beta} \frac{\partial}{\partial \xi_i} \left[\left(\frac{\rho}{\xi_{ij}} \right)^{12} - \left(\frac{\varepsilon_{\alpha\beta}}{\varepsilon_{\alpha\alpha}} \right)^{\frac{1}{2}} \left(\frac{\rho}{\xi_{ij}} \right)^6 \right] \quad (i \in \alpha) \end{aligned} \quad (\text{C-1a})$$

$$\begin{aligned} \mu \frac{d\bar{\mathbf{v}}_i}{d\tau} = & - \sum_{j \in \alpha} \frac{\partial}{\partial \xi_i} \left[\left(\frac{\rho}{\xi_{ij}} \right)^{12} - \left(\frac{\varepsilon_{\alpha\beta}}{\varepsilon_{\alpha\alpha}} \right)^{\frac{1}{2}} \left(\frac{\rho}{\xi_{ij}} \right)^6 \right] \\ & - \sum_{j \in \beta} \frac{\partial}{\partial \xi_i} \left[\left(\frac{\rho_2}{\xi_{ij}} \right)^{12} - \left(\frac{\varepsilon_{\beta\beta}}{\varepsilon_{\alpha\alpha}} \right)^{\frac{1}{2}} \left(\frac{\rho_2}{\xi_{ij}} \right)^6 \right] \quad (i \in \beta) \end{aligned} \quad (\text{C-1b})$$

The integration of these equations by numerical simulations is not much more time-consuming than integrating the equations used in Chap. IV (Eqs. (IV-3) or (IV-4)). However, Eq. (C-1) has more system parameters than Eqs. (IV-3) or (IV-4), $\varepsilon_{\alpha\beta}/\varepsilon_{\alpha\alpha}$ and $\varepsilon_{\beta\beta}/\varepsilon_{\alpha\alpha}$.

It can be noted that Eq. (C-1) approaches Eq. (IV-3) in the limit of $\varepsilon_{\alpha\beta}/\varepsilon_{\alpha\alpha} \rightarrow 0$ and $\varepsilon_{\beta\beta}/\varepsilon_{\alpha\alpha} \rightarrow 0$.

C.2 Difference between Y_{self} and Y

Figure C-1 shows the sputtering yield of surface atoms Y of the LJ system of this study for $\mu = \rho = 1$ (denoted by filled triangles; data are the same as those in Fig. IV-4) and the self-sputtering yield Y_{self} of the full LJ system of single species given in Ref. 134 (denoted by the empty circles). The solid curve, following the filled triangles, is a guide to the eye. The definitions of Y and Y_{self} are not the same and they are related via Eq. (IV-5), as discussed in Sect. IV.3.1.

It is seen that yield data of filled triangles and empty circles agree well in a high energy range of $\mathcal{E} > 100$, where we expect the sticking probability of the incident species is high, i.e., $s \simeq 1$. Under such conditions, $Y \simeq Y_{\text{self}}$. On the other hand, when the incident energy is low, the incident species cannot penetrate the material deeply and may leave the surface after impact, even if they have attractive interaction with surface atoms, resulting in $s < 1$. Therefore the difference in

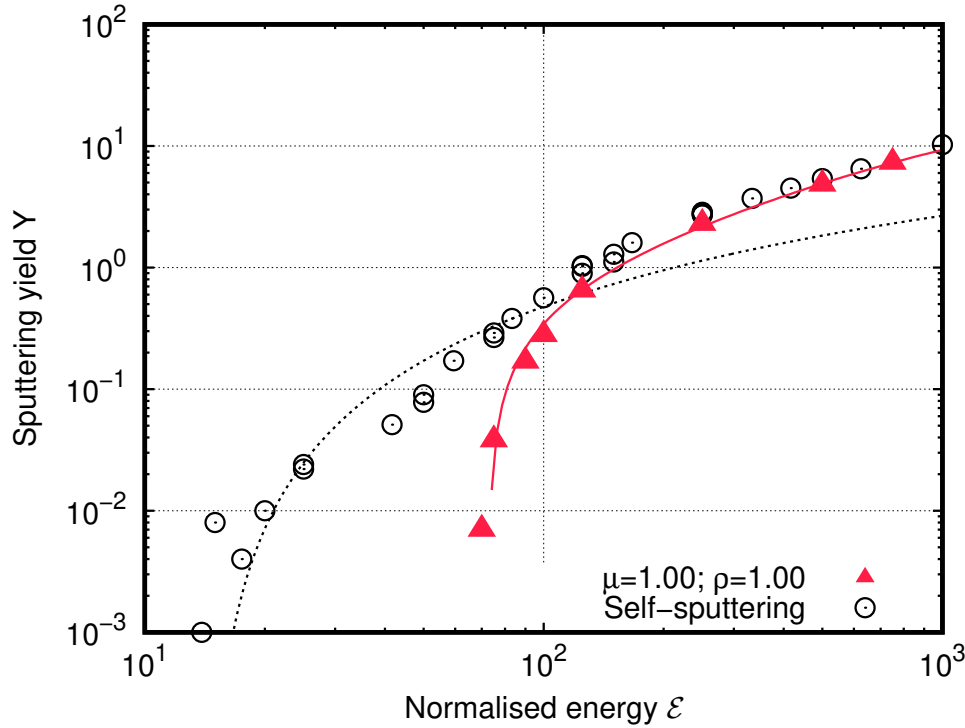


Figure C-1 – Comparison between the sputtering yield of surface atoms Y of the LJ system of this study for $\mu = \rho = 1$, denoted by triangles (as given in Fig. IV-4), and the self-sputtering yield Y_{self} of the full LJ system from Ref. 134, denoted by circles. The dashed curve is the empirical fitting functions proposed by Yamamura and Tawara for experimentally obtained self-sputtering yields of Ni given in Ref. 57.

definition between Y_{self} and Y , at least partially, accounts for the disagreement between filled triangles and empty circles at low incident energies.

This difference can also arise from the difference in interatomic potential. In the LJ system of this study, incident species react with surface atoms only repulsively whereas, in the full LJ system of Ref. 134, both incident species and surface atoms have the same full LJ potential. In the former system, incident species are unlikely to be deposited. In the latter system, if incident species are deposited and the surface structure changes, the sputtering yield may change accordingly. Discussion on such effects on the sputtering yield is out of the scope of this work and will be analysed elsewhere.

The experimental self-sputtering yields are also plotted as a dotted curve, based

on the empirical fitting curve of Ref. 57. It is seen that the empty circles show good agreement with the experimental values for $\mathcal{E} < 10$, as both represent Y_{self} . In a higher energy range of around $\mathcal{E} > 200$, the yields obtained from the LJ system are consistently higher than the experimental data. As discussed in Ref. 134, this is due to the inaccurate representation of the LJ's repulsive potential for real systems.

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Research achievements

Published papers

- 1 - N.A. Mauchamp, M. Isobe and S. Hamaguchi, Evaluation of nickel self-sputtering yields by molecular-dynamics simulation, *J. Vac. Sci. Technol. A*, **39**, 043005 (2021) [10.1116/6.0000979](#)
- 2 - N.A. Mauchamp, K. Ikuse, M. Isobe and S. Hamaguchi, Self-Sputtering of a Lennard-Jones solid, *Phys. Plasmas*, **29**, 023507 (2022) [10.1063/5.0077762](#)
- 3 - N.A. Mauchamp and S. Hamaguchi, Why are physical sputtering yields similar for incident ions with different masses? — physical sputtering yields of the Lennard-Jones system, *J. Phys. D: Appl. Phys.*, **55**, 225209 (2022) [10.1088/1361-6463/ac57dc](#)
- 4 - N.A. Mauchamp and S. Hamaguchi, Molecular dynamics simulation of Si trench etching with SiO₂ hard masks, *J. Vac. Sci. Technol. A* (*in press* 2022) [10.1116/6.0002003](#)

Oral presentations

- 1 - N. Mauchamp, M. Isobe and S. Hamaguchi, “Molecular Dynamics Simulation for Physical Sputtering of Surfaces made of Lennard-Jones Atoms”, 65th JSAP Spring meeting, Tokyo, Japan, 17-20 March 2018
- 2 - N. Mauchamp, M. Isobe and S. Hamaguchi, “Physical etching of surfaces

made of Lennard-Jones particles: Analyses by molecular dynamics simulations”, RUB Japan Science Days 2018, Bochum, Germany, 4-7 July 2018

- 3 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Physical etching of surfaces made of Lennard-Jones atom: a Molecular Dynamics study”, 79th JSAP Autumn meeting, Nagoya, Japan, 18-21 Sept. 2018
- 4 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Molecular Dynamics Study on Collision Cascade Dynamics for Sputtering of Lennard-Jones Particles”, 65th AVS Symposium, Long Beach, USA, 21-26 Oct. 2018
- 5 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Sputtering of surfaces made of Lennard-Jones atoms: A Molecular Dynamics study”, XXXIV ICPIG & ICRP-10, Sapporo, Japan, 14-19 July 2019
- 6 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Relation between atomic interaction parameters of a surface material and its physical sputtering yield; how to predict the etching rate based on the surface material properties”, 66th AVS Symposium, Columbus, USA, 20-25 Oct. 2019
- 7 - **N. Mauchamp**, M. Isobe, J. Wang, J. Kenney, S. Rauf and S. Hamaguchi, “Molecular dynamics simulations of nano-scale trench etching of Si by chlorine plasmas”, 18th International Conference on Thin Films & 18th Joint Vacuum Conference, Budapest, Hungary 22-26 Nov. 2020 (Online)

Poster presentations

- 1 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Evaluation of Nickel Self-Sputtering Yields by Molecular Dynamics”, 78th JSAP Autumn meeting, Fukuoka, Japan, 5-8 Sep. 2018
- 2 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Molecular Dynamics Simulation of Ni Self-sputtering and Modeling of Interatomic Potential Functions”, 64th AVS Symposium, Tampa, USA, 29 Oct. - 3 Nov. 2017

- 3 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Collision Cascade Dynamics for Self-Sputtering of Lennard-Jones Atoms”, 39th International Symposium on Dry Process, Tokyo, Japan, 16-17 Nov. 2017
- 4 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Molecular dynamics simulation of Ni self-sputtering and modeling of interatomic potential functions”, 82th IUVESTA Workshop, Okinawa, Japan, 4-7 Dec. 2017
- 5 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “General scaling of sputtering yields; molecular dynamics study of Lennard-Jones systems”, 40th International Symposium on Dry Process, Nagoya, Japan, 13-15 Nov. 2018
- 6 - **N. Mauchamp**, M. Isobe and S. Hamaguchi, “Evaluation of the correlation between physical sputtering yield and material physical properties using Molecular Dynamics simulations”, 41st International Symposium on Dry Process, Japan, 21-22 Nov. 2019