Development of a Multiscale Atomistic Code to Investigate Self-Organized Pattern Formation Induced by Ion Irradiation

Zhangcan Yang
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For the degree of Doctor of Philosophy

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Head of the Graduate Program Date
DEVELOPMENT OF A MULTISCALE ATOMISTIC CODE TO INVESTIGATE
SELF-ORGANIZED PATTERN FORMATION INDUCED BY ION
IRRADIATION

A Dissertation
Submitted to the Faculty
of
Purdue University
by
Zhangcan Yang

In Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

December 2013
Purdue University
West Lafayette, Indiana
To my family
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SYMBOLS

\( \theta \) \quad \text{incidence angle}

\( h \) \quad \text{surface height}

\( \Delta h(x, y) \) \quad \text{crater function}
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<td>BCA</td>
<td>Binary Collision Approximation</td>
</tr>
<tr>
<td>BH</td>
<td>Bradley-Harper</td>
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<tr>
<td>ES</td>
<td>Ehrlich-Schwoebel</td>
</tr>
<tr>
<td>EUV</td>
<td>extreme ultraviolet</td>
</tr>
<tr>
<td>IBS</td>
<td>ion beam sputtering</td>
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<tr>
<td>kMC</td>
<td>kinetic Monte Carlo</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>PBC</td>
<td>Periodical boundary conditions</td>
</tr>
<tr>
<td>PDE</td>
<td>partial differential equation</td>
</tr>
<tr>
<td>PKA</td>
<td>primary knock-on atom</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dots</td>
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<tr>
<td>RDF</td>
<td>radial distribution function</td>
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<td>SRIM</td>
<td>the Stopping and Range of Ion in Matter</td>
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<td>TRIDER</td>
<td>TRansport of Ions in matter with DEfect Relaxation</td>
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<tr>
<td>WWW</td>
<td>Wooten, Winer, and Weaire</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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ABSTRACT

Yang, Zhangcan Ph.D., Purdue University, December 2013. Development of a multiscale atomistic code to investigate self-organized pattern formation induced by ion irradiation. Major Professor: Jean Paul Allain.

Various self-organized patterns including ripples and quantum dots can be induced by ion beam sputtering (IBS). For the past decades, the understanding of such phenomenon has been mainly relied on the Bradley-Harper theory that attributes the formation of self-organized patterns to the interplay between roughening by curvature dependence of erosion and smoothening by surface diffusion. Recently, the development of the crater function theory has overturned this erosion-based paradigm to a redistribution-based paradigm. The theory has proved that erosion is irrelevant and negligible in the pattern formation at low and intermediate incidence angles. Despite the success, there are still some questions open to discuss. The role of erosion for the ripple formation at glancing angles is still unclear. Furthermore, the current application of the crater function theory is limited in the linear regime. The applicability in the nonlinear regime is unknown. In this work, a hybrid MD/kMC (Molecular Dynamics/kinetic Monte Carlo) multiscale atomistic model is developed to elucidate these unknown issues. This model uses the crater functions, which are obtained by MD simulations, to model the prompt mass redistribution due to single-ion impacts. Defect migration, which is missing in previous models using crater functions, is treated by a kMC Arrhenius model. Using this model, a systematic study was performed for silicon bombarded by Ar$^+$ ions of various energies (100 eV, 250 eV, 500 eV, 700 eV and 1000 eV) at incidence angles of 0° to 80° with fluence up to $10^{18}$ ions/cm² to cover both the linear and nonlinear regimes. The simulation results are in very good agreement with the experimental findings and the moment-description
continuum theory in many features of surface evolution, namely, the phase diagram, wavelength dependence of ion energy and incidence angle, and the nonlinear evolution of surface roughness. The simulations elucidate that erosion plays the dominant role in the pattern formation at glancing angles. In the nonlinear regimes, the ripples first undergo coarsening and then reach saturation state. The surface roughness obeys the scaling theory and yields the growth exponent $\beta = 0.358$, which is very close to the experimental finding. Ion irradiation with simultaneous sample rotation is also simulated, resulting in the formation of arrays of squared ordered dots. The patterns with sample rotation are found to be strongly correlated to the rotation speed and the pattern types formed without sample rotation.
1. INTRODUCTION AND MOTIVATION

1.1 Self-organized nanostructures by ion beam sputtering (IBS)

1.1.1 Advantages and disadvantages of IBS

Nanofabrication, as one of the key bases for nanoscience and nanotechnology, is the process of making nanostructures with minimum dimension smaller than 100 nm [1–3]. For decades, enormous efforts have been devoted to increase the resolution and decrease the cost of nanofabrication techniques, in order to make more components in a unit area with reasonable cost. In general, the techniques used in nanofabrication can be divided into two categories “top-down” and “bottom-up” based on the way to fabricate patterns. The top-down techniques use lithography methods to fabricate structures, as depicted in Figure 1.1. The conventional optical lithography technique, known as the most established nanofabrication tool and commercially available, has pushed to its limit (resolution \( \sim 50 \) nm) due to the diffraction effect [1, 3, 4]. For resolution enhancements, various methods have been proposed. For example, EUV (Extreme Ultraviolet) lithography uses soft X-rays (\( \lambda \sim 13.5 \) nm) to achieve sub-50nm resolution [5–7]. Scanning beam lithography uses electron beam or focused ion beam rather than light as the exposure source in order to overcome the diffraction limit of light [8, 9]. It is capable to pattern features with resolution down to \( \sim 20 \) nm [1]. However, these methods are still under development and their future for commercially massive application is still uncertain due to demerits, such as, not cost-effective, slow in fabrication or not capable for large area manufacture [3].

In contrast to the top-down techniques, the bottom-up techniques fabricate structures by the self-assembly or self-organization of atoms, driven by the interactions between atoms. Ion beam sputtering (IBS) is a commonly known technique that can
Figure 1.1.: Sketch showing the procedure of fabricating patterns in hard materials by optical lithography technique. The substrate Si/quartz surface is coated with a layer of photoresist. The desired pattern can be either written directly to the photoresist by a scanning beam or by exposed to a light source, with a mask placed between them. The exposed photoresist is immersed into solvents to dissolve the exposed (positive photoresist) or unexposed (negative photoresist) regions, leaving patterns on photoresist for the access of the substrate surface. The patterned photoresist then undergoes either dry etch or film deposition to transfer the patterns to the substrate. (Image taken from [1])
induce self-organized patterns at nanoscale on various materials. When a solid surface is bombarded by low-energy ion beams, self-organized nanoscale features (e.g., holes, periodic ripples, or highly ordered dots) can be produced under suitable irradiation conditions [10–17]. This spontaneous formation of nanopatterns has intrigued many researchers due to its potential application to fabricate nanostructures and to create sublithographic templates for making the next generation of electronic devices [18].

IBS possesses a few advantages over other nanofabrication techniques. First of all, it is a scalable, parallel nano-manufacturing process that is capable to grow nanostructures in a large area in a one-step, clean process with low cost. This is distinct from the lithography techniques. Fabrication by lithography techniques takes a serial steps, including production of optical mask, coating of photoresist layer, exposure to light source, dissolution of photoresist, and etching or deposition, as illustrated in Figure 1.1. Among these steps, making optical mask is usually the most expensive part. Dissolving the photoresist sometimes causes introduction of contamination issue. In comparison, self-organized structures induced by IBS is performed simply by exposure of the target material to ion beam in a vacuum chamber, as shown in Figure 1.2. Using a broad ion beam with a typical ion flux $\sim 10^{15} \text{cm}^{-2}$, it is able to pattern an area of 1 cm in a few minutes. During the whole process, no other chemical can be in contact of the sample wafer since the whole process is in vacuum.

Secondly, metastable nano-phases introduce completely new classes of materials at the surface without affecting bulk properties. Ions only penetrate a monolayer to hundreds of nanometers into the surface depending on their energy. The ions bring energy into a system and can drive the system far away from equilibrium, where the materials can exhibit unique properties. Also, the ions do not only change the topography of the surface, but also its chemical and mechanical properties. This has stimulated studies to find surface applications for medical implants, photovoltaics, sensors, etc [17,20,21]. The process is also is applicable to a wide range of materials, including metals, semiconductors, insulators and polymers [15–17,22–24].
Last but not least, a variety of patterns can be formed just by tuning ion energy, incidence angle, temperature and other experimental parameters. When an ion dissipates its energy in the target material, it collides with target atoms, causing displacement of atoms, creation of defects, and ejection of atoms from the surface. As a consequence, the surface height around the impact point is changed due to sputtering and mass redistribution. Both the amount of sputtered atoms and mass redistribution depend on a number of ion and target parameters, particularly the local incident angle and the surface curvature. This leads to differences in surface responses at different local regions, eventually resulting in formation of different structures. In light of this, a variety of patterns can be obtained by using different ion and target parameters. Figure 1.3 give a few examples of diversity of patterns forming on Si and Ge surfaces by low-energy ion-beam bombardment [15]. We see a variety of patterns such as holes, dots, and ripples with varied degrees of ordering. These patterns exhibit the remarkable capacity of ion irradiation in making various nanostructures. However, this variety also shows the significant difficulty of deciphering surface evolution under ion bombardment.
Figure 1.3.: Examples of diversity of pattern formation: (a) ultra smooth surface, (b) randomly arranged holes, (c) randomly arranged troughs, (d) short range hexagonally ordered dots, (e) highly aligned ripples, (f) coexistence of short ripples and dots, (g) squared ordered dots, (h) long range hexagonally ordered dots, and (i,k,l,m) fingerprint-like curved ripples. The irradiation conditions for these patterns were ion energies between 500 eV and 2000 eV, ion species of Ar\(^{+}\), Kr\(^{+}\) and Xe\(^{+}\), between incidence angles of 0° and 75°, and some samples were rotated simultaneously with irradiation. This figure is taken from [15].

There is one thing to note here. At the time when these patterned were reported, the effects of impurities had not been drawn into attention, since most of the impurities are introduced by accident, e.g., the sample clips. Ozaydin and coworkers [25–27] found that the existence of Mo impurity can change the surface pattern dramatically. Without impurities, a silicon surface tends to remain flat under normal incidence [25,28]. The lack of XPS (X-ray photoelectron spectroscopy) or other com-
Positional characterization data in [15] makes it difficult to judge if any impurities were involved.

In recent decades, more and more attention has been drawn to binary compound materials or multiple elemental systems. In 1999, Facsko and coworkers [12] observed the formation of ordered quantum dots on the compound semiconductor GaSb by normal incidence of 420 eV Ar\(^+\) ions. The size and the spacing of these dots are controllable by tuning the experimental conditions, such as ion energy. Ordered dots have also been created on Ge, InP and other group III-V semiconductor materials by ion irradiation, which demonstrates that ion irradiation can be a controlled and cost-effective method to produce well-ordered quantum dots (QD) [29–31].

There are also several shortcomings of IBS compared to nanolithography techniques. Although IBS is capable of fabricating ordered, repeated structures on a large area, it is not able to fabricate arbitrary structures. This essential shortcoming comes with the self-organization nature. As a result, it is difficult to overcome. Another major drawback is the present of defects in the nanostructures. Figure 1.4 shows possible defect types in sputtered ripples (A) and hexagonal dots (B). In Figure 1.4(A), the well aligned ripple structures are ruined by the join of two ripples (L1) or the termination of a ripple (L2). Figure 1.4(B) shows four different types of defects that destroy the ordering of the hexagonal dots. Most of the dots are with six nearest neighbors. However, there are some dots missing (D1 and D2), and some dots are surrounded by five or seven neighbors (D3 and D4). These defects will inhibit the application for making electronic devices. The suggested solution to overcome this shortcoming is to combine the lithography technique and ion beam sputtering. Cuenat and coworkers used pre-patterned surface and succeeded to improve the long-range order of the ripples significantly [32], as shown in Figure 1.5. The left part of Figure 1.5 is the ripple structures formed on a flat surface. The ripples exist a high density of defects. However, the ripples formed between the pre-patterned surface are with almost no defects (right part of Figure 1.5).
Figure 1.4.: Examples of defect types in (A) ripples of silicon bombarded by 1200 eV Kr\(^+\) at 15°, and (B) hexagonally ordered dots of GaSb induced by 500 eV Ar\(^+\) ions. L1 and L2 point to the join of two ripples and termination of a ripple, respectively. D1 and D2 indicate a missing dot (vacancy) surrounded by six and five nearest neighbors, respectively. D3 and D4 show a dot with five and seven nearest neighbors, respectively. (Image modified from [15] and [33]).

Figure 1.5.: Comparison of ripple alignment outside (left) and inside (right) of lithographically templated region. The image is taken from [32].

1.1.2 Applications of ion-induced patterning

Researchers have reported quite a few applications for ion-induced nanostructures in literature. Munoz-Garcia and coworkers [17] provide a very good summary, suggesting fields in optical devices, DNA separation, quantum dot (QD) arrays fabrications, film deposition and etc. Here, only a few relevant applications to our research
group are presented. The first is the fabrication of QD arrays on given materials by pattern transferring [29]. Figure 1.6 shows schematically the principle of transferring quantum dots of GaSb on an AlSb layer. At first, a thin film of GaSb is deposited on a different substrate (AlSb) by molecular beam epitaxy (MBE). Then, 420-eV Ar$^+$ ions are used to bombard the GaSb layer at normal incidence. Regular ordered GaSb quantum dots would be formed under such irradiation conditions [12]. Irradiation is continued until the AlSb layer is just exposed. At this point, the GaSb dots are left on the top of the AlSb substrate.

Figure 1.6.: Schematic drawing of producing quantum dots arrays by transferring ion-induced nanodots. Figure adapted from [29]

Ion-induced nanostructures can also be used in the area of biomaterials. Patterned nano and microstructured surfaces have been found to increase cell adhesion because of their influence on surface wettability, increased surface area, and cell shape [34–36]. Both the topography of the nanopatterned surface and its surface chemistry play a critical role in cell functions including regulation of growth factor signaling and intracellular signaling important for proliferation and reconstruction of endovascular tissues [37]. Nanostructures also improve cell growth by acting as directional cues. Cells are often directed through the ridges/grooves of the nanostructures and will align themselves with the direction of these ridges. Nanostructures, mimicking the naturally occurring extracellular matrix (ECM), provide support and anchorage for cells as well as directional cues. Since IBS can produce surfaces with various roughnesses and patterns, it provides a way to investigate how cell response to different
nanostructures, and it becomes possible to control the biocompatibility of biomaterials by creating nanostructures and modification of chemistry on the surface using an ion beam [21].

1.2 Existing theories and their limitations

Since the discovery of pattern formation by ions irradiation in 1962 [10], various theories have been proposed to explain this phenomenon. This section gives a summary, along with the advantages and limitations, of the major existing theories on this topic. Due to the scope of this work, we only discuss theories for single elemental materials bombarded by noble gas ions.

1.2.1 Sputtering theory

In order to model surface evolution under ion bombardment, it is important to understand the fundamentals of ion-material interaction first. The first record of sputtering in the laboratory was reported by W. R. Grove in 1852 [38]. For more than a century after the discovery, the ejection of atoms from solid surfaces under ion bombardment was thought to be the result of a thermal evaporation. This point of view was changed as more and more data were produced in 1950s. The concept of collision cascade was accepted by more and more researchers and a large number of sputtering experiments could be accounted for using collisional concepts.

A collision cascade is produced by the interaction of ions with the lattice atoms. As shown in Figure 1.7, the incidence ion transfers its kinetic energy to a lattice atom. If the transferred energy is higher than the threshold displacement energy of the target material (usually a few tens of eV), the atom will be displaced from the lattice site to create a primary knock-on atom (PKA), leaving a vacancy at the site. The PKA then causes additional knock-on atoms. As a result, the serial of collisions of atoms produces a displacement cascade. The termination of cascade results in individual vacancies and interstitials. Collision cascade at the near surface region
often leads to sputtering. If a recoil reaches the target surface with an energy larger than the surface binding energy, the recoil can be ejected from the surface.

In 1955, Kinchin & Pease published their famous theory on displacement damage [40], which derived a formula to calculate the number of Frenkel pairs \( N_d \) as

\[
N_d = \frac{E}{2E_d} \tag{1.1}
\]

where \( E \) is the kinetic energy of the primary recoil atom, and \( E_d \) is the displacement threshold energy. Later, Thompson (1968 [41]) and Sigmund (1969 [42]) successfully derived linear transport equations to calculate the sputtering yield and the energy spectra of the sputtered atoms that result from the bombardment of ions on random targets. These two works are known as the “classic sputtering theory”. The classical sputtering theory has undergone extensive experimental testing and gained great success. According to the sputtering theory, the yield is given by

\[
Y = \Lambda F_D \tag{1.2}
\]

where \( F_D \) is the energy deposited per unit depth that is determined by the stopping power, target/ion mass ratio, the ion energy and incidence angle. \( \Lambda \) is the target
material constant depending on the surface binding energy and the collision cross section. Sigmunds sputtering theory is extremely important to the theories of surface evolution, since most of the theories are based on it.

1.2.2 Continuum theories for surface evolution

Analytical continuum theory models materials as continuous masses rather than discrete particles. It uses partial differential equations (PDE) to model the physical processes involved in surface evolution. Each term in the PDEs represents a specific process that governs the surface morphology. The continuum theory is a powerful tool and helps to interpret the experimental results. In this section, we will introduce the existing continuum theories of ion-induced pattern formation.

To begin with, consider an \( x-y \) plane that is parallel to the target surface, with the height \( h \) at point \( (x, y) \) at time \( t \) being denoted as \( h(x, y, t) \). Essentially, surface evolution is a two spatial dimension problem. To simplify the discussion, the problem can be first examined in one dimension, and expanded to 2-dimension (2D) later.

In one dimension, we denote the surface height \( h \) as a function \( h = h(x, t) \). The \( x \)-axis is parallel to the projection of the ion beam. The reference system is illustrated in Figure 1.8. The \( X-Z \) axes represent the global reference system. The \( x'-z' \) axes represent the local reference system for single ion bombardment. \( \theta \) and \( \phi \) are the global incidence angle and the local incidence angle, respectively.

The surface evolution over time can be expressed as

\[
-
\frac{\partial h}{\partial t} = V \sqrt{1 + \left( \frac{\partial h}{\partial x} \right)^2}
\]

(1.3)

where \( V \) is change speed of the surface height normal to the local surface, and \( \frac{\partial h}{\partial x} \) is the local slope (see Figure 1.8). \( V \) is a function of the local surface slope, surface curvature, and etc. In general, \( V \) consists of two parts distinguished by their different duration of time \([43]\)

\[
V = V_p + V_g
\]

(1.4)
The prompt part $V_p$ is the quick response ($\sim 10^{-11}$ s) due to ion impact. The gradual part $V_g$ includes the relaxation processes which can be on the order of minutes (up to $10^2$ s). Then, what remains is to derive the analytical form for $V$. Different theories use different methods to derive $V$.

**Bradley-Harpers linear instability theory and its extensions**

The first analytical form was developed by Bradley and Harper [11] based on Sigmunds sputtering theory [42]. This theory considers erosion or sputtering as the only cause for prompt surface response. According to Sigmunds sputtering theory, the energy deposited at point $(x', y', z')$ can be described by Eq. (1.5) as a Gaussian ellipsoid (Figure 1.9)

$$E(r) = \frac{\epsilon}{(2\pi)^{3/2}\sigma\mu^2} \exp\left(-\frac{[z' + a]^2}{2\sigma^2} - \frac{x'^2 + y'^2}{2\mu^2}\right)$$

Here $\epsilon$ is the energy of incidence ion, $a$ is the average depth of energy deposition, and $\sigma$ and $\mu$ are the widths of the distribution parallel and perpendicular to the ion trajectory, respectively. The possibility of an atom at the surface to be sputtered is proportional to the energy deposited at that point. As a result, $V_p(x)$ can be
calculated by integrating the erosive contributions over all nearby impacts, yielding in 1D:
\[ V_p(x) = \int C \cdot E(x, x') dx' \]  \hspace{1cm} (1.6)

The constant \( C \) is related to the local ion flux and the properties of the target material, particularly, the surface binding energy, and \( E(x, x') \) is the amount of energy deposited at point \( x \) for an ion impact at point \( x' \).

Figure 1.9.: Ellipsoidal shape of energy deposition profile. The probability of a surface atom at \((x', y', z')\) to be sputtered is proportional to the energy deposited at this points.

By assuming the slope of the surface is small enough, Eq. (1.3) can be approximated as:
\[ -\frac{\partial h}{\partial t} \approx V \]  \hspace{1cm} (1.7)

Eq. (1.6) can be integrated by inserting Eq. (1.5); the detailed derivation of integration is omitted here. Meanwhile, the surface is assumed to relax by thermal activated surface diffusion. Including the diffusion part, the resulting partial differential equation (PDE) can be simply written in a linear form as
\[ \frac{\partial h}{\partial t} \approx -V_0 + S \frac{\partial^2 h}{\partial x^2} - B \frac{\partial^4 h}{\partial x^4} \]  \hspace{1cm} (1.8)
where the first term on the RHS (right hand side) is the average erosion rate. the second term describes the curvature dependence of sputtering yield, and the third term describes the thermally activated surface diffusion.

The BH theory attributes ripple formation to the interplay between curvature-dependent sputtering and surface diffusion. The stability of the surface under a small perturbation can then be examined. Since Eq. (1.8) is linear, any perturbation can be written as superposition of the sine perturbation, which can be written as

\[ h_q(t) = A \exp(\omega t) \exp[i(qx)] \]  (1.9)

where \( A \) represents amplitude; \( q \) is the wavefactor; and \( \omega \) is the exponent factor of the growth rate of the perturbation. Inserting Eq. (1.9) into Eq. (1.8) and neglecting the constant erosion term \(-V_0\), it yields:

\[ \omega = -S q^2 - Bq^4 \]  (1.10)

\( \omega \) reaches its maximum value when \( q^* = \sqrt{\frac{S}{2B}} \). The maximum \( \omega \) represents the fastest growth of perturbation. Thus, BH theory predicts that the characteristic wavelength of resulting ripples is \( \lambda^* = \frac{2\pi}{q^*} = 2\pi \sqrt{\frac{2B}{S}} \).

Calculation of the coefficient \( S \) shows that \( S \) is always negative, which means the surface is unstable to any perturbation. In other word, BH theory predicts ripple formation for all inclined angles. Furthermore, BH theory predicts a transition of ripple orientation from parallel mode to perpendicular mode at glancing angles.

The linear B-H model is a rather successful model for explaining and predicting some features of the ripple formation in the early stage, as described above. However, some experimental observations have shown contradictions with BH model [44–47]. Particularly, observations of a smooth regime for low incidence angles (< 45°) have triggered doubts about the validity of Eq. (1.6), because erosion is not the only contribution to prompt surface height change. Ion-stimulated mass transport can also result in morphology change [47].

There are other intrinsic limitations of BH linear theory originated from its simplifications and assumptions. For instance, the theory is only valid for early stages
due to its use of the small slope approximation. As the amplitude of the results grow larger, the small slope assumption breaks down. The linear model predicts that the amplitude of the ripples increases exponentially with time. In experiments, however, the amplitude of the ripple reaches saturation under a certain amount of irradiation. Additionally, the BH model uses thermally activated surface diffusion as the surface relaxation process, which is only valid for high temperature and low flux. At low temperatures, thermally activated diffusion is almost nonexistent and other modes of relaxations, such as ion-induced diffusion [14, 48] or ion-enhanced viscous flow [49, 50], dominate.

Many efforts have been made to enhance the BH linear theory to overcome its limitations and drawbacks. Cuerno and Barabasi [51] included a Gaussian white noise term to account for the stochastic arrival of ions. Also, they expanded Eq. (1.3) and obtained a nonlinear term $\left( \frac{\partial h}{\partial x} \right)^2$ to account for amplitude saturation at late stage. They showed that, at long times, the nonlinear term dominates in morphology evolution. Makeev and coworkers [14, 48] also expanded $V$ in powers of slope, but to higher order. They obtained a fourth order term $D \frac{\partial^4 h}{\partial x^4}$, which is called “effective surface diffusion”. They demonstrated that in addition to relaxation by thermal diffusion, the effective surface diffusion induced by ions also contributes to the smoothing mechanism. Another significant enhancement is the inclusion of the mass redistribution effect, which will be discussed in the next section.

**Crater function theory**

Ripple formation is not the only consequence of ion beam bombardment. Absence of ripples on Si bombarded by Xe$^+$ at angles between 0° and 45° was observed by Carter and Vishyakov [44], and ultra-smooth carbon surfaces have been found for self-bombardment of carbon coatings [52]. Madi and coworkers reported that ultrasmooth stable silicon surfaces were achieved by various energies of Ar$^+$ ions irradiation at angle < 47° (see Figure 1.10) [47, 53]. These observations are contradictory to BH
theory, which always predicts ripple formation at all inclined angles. Thus, other mechanisms beyond the ones proposed by BH theory and alternatives have to be employed to explain ion-induced ultra smoothening.

Figure 1.10.: Phase diagram of pattern formation of Ar$^+$ ion beam sputtering of nominally room temperature Si(001) in the linear regime of surface dynamics in the absence of secondary scattering effects. ×: flat; □: parallel mode ripples; ○: perpendicular mode ripples. Fluence is $3.8 \times 10^{18}$ Ar$^+$ cm$^{-2}$ for flat stable surfaces and $3.2 \times 10^{17}$ Ar$^+$ cm$^{-2}$ for parallel and perpendicular mode ripples at $\theta \geq 50^\circ$. Taken from [47, 53].

Carter and Vishyakov were the first to propose the idea of collision-induced mass redistribution to explain the absence of ripples of Si under Xe$^+$ bombardment at angles between 0$^\circ$ and 45$^\circ$. They invented a new term to describe the mass redistribution effects [44]. Moseler and coworkers proposed an atomistic/continuum multiscale model [52]. They calculated the impact-induced average change of the local surface profile, using molecular dynamics (MD) simulations, which was like a crater at nanoscale. Then, they found that carbon ion impacts induce downhill currents,
which erode hills into nearby hollows. They concluded that lateral mass transport, rather than sputtering, is the dominant force that determines surface morphology. Attention has begun to be paid to the surface mass transport induced by ion beams, especially the crater-shaped surface profile caused by single ion impacts.

Recently, Norris and coworkers derived the first analytical form of the continuum equation which was given in the form of crater moments [43,54]. Here, a brief summary of the model and its major outcomes is presented. Let the crater function $\Delta h(x-x', \theta)$ represent the average change of local surface height at $x$ due to single ion impact at $x'$, with incidence angle $\theta$. The prompt contribution to surface evolution, i.e., Eq. (1.6), can be modified to give (in 1D)

$$V_p(x, \theta) = \int \Delta h(x-x', \theta)dx'$$  \hspace{1cm} (1.11)

Now, $V_p(x)$ can be expanded in respect of a small parameter $\epsilon$, which describes the ratio of impact scale to pattern scale. The detailed mathematical derivation can be found in [43,54]. Finally, an analytical form can be obtained (in 2D):

$$\frac{\partial h(x,y,t)}{\partial t} = \left( S_X(\theta) \frac{\partial^2 h}{\partial x^2} + S_Y(\theta) \frac{\partial^2 h}{\partial y^2} \right) - B \nabla^4 h$$  \hspace{1cm} (1.12)

where the coefficients are given by

$$S_X(\theta) = I_0 \frac{d}{d\theta} [M^{(1)}(\theta) \cos(\theta)]$$  \hspace{1cm} (1.13a)

$$S_Y(\theta) = I_0 M^{(1)}(\theta) \cos(\theta) \cot(\theta)$$  \hspace{1cm} (1.13b)

$$B = \frac{\gamma d^3}{3 \eta}$$  \hspace{1cm} (1.13c)

where $I_0$ the ion flux; $M^{(1)}$ is the first moment of the crater function and is defined as

$$M^{(1)}_x(\theta) = \iint \Delta h(x,y)xdxdy$$  \hspace{1cm} (1.14a)

$$M^{(1)}_y(\theta) = \iint \Delta h(x,y)ydydx$$  \hspace{1cm} (1.14b)

$M^{(1)}$ represents the magnitude and direction of net mass movement; the parameter $B$ is the coefficient of ion-enhanced viscous flow [50]; $\gamma$ is the surface free energy; $d$ is the thickness of the thin amorphous layer; $\eta$ is the viscosity of the amorphous layer.
The same instability analysis as done for BH linear theory in Section 1.2.2 can be performed. The signs of $S_x$ and $S_y$ determine the stability and instability of the surface to perturbations. If both $S_x$ and $S_y$ are positive, then the surface is stable to any perturbation, which means the surface would remain flat under irradiation; If either $S_x$ or $S_y$ is negative, then the surface is unstable to any perturbation, leading to ripple formation.

The signs $S_x$ and $S_y$ are determined by the first moment of crater function. Specifically, since $M_y^{(1)}$ is zero for all incidence angles due to symmetry, the calculation of $S_x$ and $S_y$ can be reduced to

$$S_x(\theta) = I_0 \frac{d}{d\theta} [M_x^{(1)}(\theta)\cos(\theta)]$$  \hspace{1cm} (1.15a)

$$S_y(\theta) = I_0 M_x^{(1)}(\theta)\cos(\theta)\cot(\theta)$$  \hspace{1cm} (1.15b)

$$M_x^{(1)}(\theta)$$  \hspace{1cm} (1.15c)

It is clear that $\frac{d}{d\theta}[M_x^{(1)}(\theta)\cos(\theta)]$ determines the sign of $S_x$, and $M_x^{(1)}(\theta)$ determines the sign of $S_y$. Hence, the critical incidence angle between stability and instability regimes can be acquired by calculation of $M_x^{(1)}(\theta)$.

This moment-based theory was used to study Si irradiated by 100 eV and 250 eV Ar$^+$ [43]. Figure 1.11 shows the coefficients $S_x(\theta)$ and $S_y(\theta)$ calculated for the 250-eV case. In order to compare sources of contribution, the erosive part (i.e. contribution from pure sputtering) and redistributive part (i.e. contribution from mass transport, excluding sputtering) are also calculated separately. Two main conclusions can be drawn from the data. First, there is a flat-to-ripple transition at around 40° due to the sign of $S_x$ changing from positive to negative at $\theta = 40^\circ$. Although the experiment has observed the transition near 50° [47], it is a significant improvement compared to BH linear theory. Second, the contribution of erosive effects to the coefficient $S$ is about an order of magnitude smaller than the redistributive effects. In other word, it is the mass redistribution, rather than erosion, that determines if the surface is flat or forms ripples. This conclusion completely changes the traditional view that considers erosion to be the main mechanism dominating surface pattern formation.
Figure 1.11.: Coefficients $S_x$ and $S_y$ for Si irradiated by 250-eV Ar\textsuperscript{+} calculated using Eq. (1.15). The erosive contribution and the redistributive contribution are calculated separated for comparison. Image is taken from [43]

1.3 Motivation and Objectives

1.3.1 Unresolved problems

Despite lots of efforts on experiments and theories in modeling ion-induced nanostructures for the past few decades, there are still many basic questions open to discussion. For example, even though the inclusion of mass redistribution provides a convincing explanation for flat-to-ripple transition [43], the underlying mechanism for the transition of ripple orientation at glancing angle is still in question. The traditional BH theory asserts that the curvature dependent erosion determines ripple orientation [11]. The mass redistribution based theory did not predict a transition to perpendicular-mode ripples at high angles, which was suggested to be due to the absence of any curvature dependence of sputtering yield, shadowing effects or surface channeling in the model [43]. Although Hossain and coworkers [55] asserted that mass redistribution is able to explain formation of perpendicular-mode ripples at glancing angles, the incorrect prediction of perpendicular-model ripples at small angles, which was reported in experiments [28] but later corrected due to multiple scattering effects [53], makes their conclusion open to debate. Thus, the moment-based theory is
not the ultimate answer to surface evolution under ion bombardment and the role of sputtering in ion-induced pattern formation remains a matter of speculation.

Furthermore, the recently developed moment-based theory by Norris has additional shortcomings. Firstly, it is only valid for the early stage bombardment due to assumption of small slope of the surface and truncation of expansion to first order. As the surface becomes rougher, the nonlinear terms or higher order terms may become important. For instance, the current moment-based theory cannot predict ripple amplitude saturation or ripple coarsening at late stages. Secondly, the current continuum theories cannot easily model pattern formation on arbitrary surfaces. In most experimental studies, smooth commercial wafers are used. However, for practical applications, the initial surfaces may be either smooth or already have features. For the latter cases, the linear continuum theories are not applicable due to the breakdown of small slope assumption. For instance, Cuenat and coworkers investigated the influence of pre-patterned surface in improving the long-range order of the ripples \cite{32}. They found that the alignments of the ripples are greatly enhanced on the pre-patterned surface, as mentioned in Section 1.1.1. The combination of lithography and ion beam technique has great value for practical usage, since technological applications, especially, fabrication of large area of electronic devices, require long-range order. However, as pointed out by Aziz \cite{46}, no theory can predict the lateral templating effect. Thirdly, the absence of shadowing effects and redeposition in existing continuum theories has weakened their validity for glancing incidence angles or steep, tall structures. Last but not least, the continuum theories ignore the surface defect kinetics under irradiation, which have been demonstrated to play an important role in surface morphology evolution \cite{19, 56–58}.

1.3.2 Objectives of this dissertation

This work aims to address the unresolved problems as discussed above. The essential shortcoming of continuum methods is that they treat the surface as a continuous
mass, which ignores the discrete nature of the surface physical processes. This in-
spired the idea of developing a discrete or atomistic model to overcome the drawbacks
of the continuum methods. In this work, a fully atomistic model is proposed, aim-
ing to study temporal (both early and late stages) evolution of ion-induced surface
morphology for primitive heterogeneous surfaces.

In general, the model is an MD/kMC hybrid model. The model treats individual
ion impacts using crater functions, which are obtained from MD simulations. Kinetic
Monte Carlo (kMC) method is used to model the ion-enhanced surface diffusion.
Specifically, the objectives of the model are:

1. Establish a reliable way for obtaining crater functions;

2. Decipher the role of sputtering in pattern formation;

3. Validate Norriss theory in the linear regime;

4. Study the ripple growth in non-linear regimes;

5. Study ripple growth on heterogeneous surfaces;

6. Study the effect of sample rotation on IBS patterning.

1.4 Outline of this work

This dissertation is organized as follows. Chapter 2 explains the choice of simula-
tion method and gives an overview of existing atomistic models. Chapter 3 explains
each part of the model and the implementation. Chapter 4 summarizes the results of
obtaining crater functions from MD simulations and analyzes the results of sputtering
yield. Chapter 5 discusses the simulation results. The model is used to study Si sur-
face evolution under 100, 250, 500, 700 and 1000 eV Ar\(^+\) bombardment at different
angles of incidence. The results are compared with continuum theory and experi-
ments. Chapter 6 concludes this work, and discusses the limitations of the model as
well as the directions for future work.
2. EXISTING ATOMISTIC MODELS

As an alternative to continuum methods, atomistic computational models possess a few advantages. This chapter will give an overview of the atomistic models that have been performed previously to model the evolution of surface morphology under ion bombardment.

2.1 Multiscale nature of ion-induced self-organized pattern formation

The difficulty to fully understand ion-induced surface evolution is mainly due to the huge time- and spatial separation of the concurrent physical processes involved in pattern formation [59], as illustrated in Figure 2.1. When a low-energy ion (eV to a few keV) impinges a target surface, it transfers its momentum mainly through nuclear collision to the recoil. If the recoil gains energy larger than threshold displacement energy, it can be displaced to become a moving atom, leaving a vacancy at the spot. The ion and the displaced atoms then continue to collide with other atoms until they become rest, creating a serial of collisions, which is called “collision cascade”. If the recoil reaches the surface with energy larger than the surface binding energy, then the recoil is ejected or sputtered permanently from the surface. A rapid quenching of the cascade is followed, leading to recombination of defects and termination of collision cascade. All of these happen in a very short duration of time ($\sim 10^{-11}$ s) and in a very small area ($\sim 10^{-9}$ m). This is only for single impact. Surface evolution under ion irradiation is a cumulative result from continuous bombardments. Typically, it takes minutes to hours ($10^2 - 10^4$ s) to irradiate a target in order to form nanostructures. Also, the surface relaxation processes are gradual processes, which are on much longer time scale ($\sim 10^{-6}$ s). As a result, a successful model needs to cover time scale from $\sim 10^{-11}$ to $10^2$ s, which spans 13 orders of magnitude.
Figure 2.1.: A sketch illustrates the multiscale nature of surface morphological evolution under ion bombardment.

In the spatial view, the target interaction with single ion impact occurs within a region of size about a few nanometers. In comparison, the typical wavelength of the ripples is in the order of tens of nanometers. Consequently, in order to observe well the growth and other interesting features of the ripple formation, the lateral size of the simulation surface should be at least a few times of the typical wavelength of ripples.

2.2 Simulation methods

The morphological evolution is a complex problem of multiple time and spatial scale. The choice of a proper simulation method is crucial. Figure 2.2 illustrates the spatial and time capacity of existing simulation methods in area of solid state. The \textit{Ab initio} method, or called the first principle method, is used to calculate electronic structures of a system by solving Schrodinger equation using the Born-Oppenheimer approximation \cite{60}. Due to its computational intense, it can only apply to a very small system (\sim a few hundred atoms) in small time scale (\sim ps), which is far smaller than our requirement. As to the field of our interest, the \textit{ab initio} methods are usually
used to calculate the interatomic potential between ion and target atoms \[61\], or the energy barrier for the diffusion process \[62\].

![Diagram showing coverage of different modeling methods in terms of time and space.](image)

Figure 2.2.: Coverage of different modeling methods in field of solids in terms of time and space.

The classical MD (Molecular Dynamics) method simulates the movement of atoms by solving the Newtonian equation of motions based on the interatomic potential. The interatomic potential only relies on the position and bonding of the atoms. If provided by proper interaction potential, MD is able to simulate ion-material interaction to an extent of good approximation. Even though classical MD is much less computationally intense than ab initio method, it can only handle systems with size $\sim 100$ nm and simulation time $\sim 1$ ns due to limited computational resources that one can access. In the radiation related filed, MD simulations are widely used to study problems like defect formations and irradiation damage. As for surface evolution under ion bombardment, Sule and Heining \[63\] reported MD simulation of ripple growth when prepatterned Si ripples were bombarded with ions. However, their initial targets are
prepatterned stripes, instead of a flat surface. The reason is that MD methods cannot simulate the whole process of ripple formation due to spatial and time limitation. In most studies, only a portion of time period can be simulated directly. As a result, the usage of MD simulations in this field is usually to obtain collision parameters or diffusion parameters for continuum theories [64–71].

The kMC (kinetic Monte Carlo) method is the bridge filling the gap between continuum method and MD method. MD method can only reproduce the dynamics of a system for less than $10^{-7}$ s. Slow thermally-activated processes, such as diffusion, cannot be modeled. Alternatively, the kMC method extends the time scale of atomistic simulations and has been widely used to study kinetics of slow processes that usually take place in an infrequent-event system. Figure 2.3 shows a schematic illustration of an infrequent-event system. The curved lines represent the energy contour. The vibrating particle is trapped in the basin of the energy surface over many vibrational periods (the red line represents the trajectory of the particle). At some point in time, when the particle gains enough energy, it finds a way to escape the basin, passing through the saddle point and entering to a new state. By realizing this, the kMC method models a slow process by carrying out the transitions, with ignoring the long time period of particle residing in an energy basin. KMC method has been successfully used in modeling surface diffusion in many studies [72–75]. The major limitation of kMC method is that all possible events and their rates have to be specified and known in advance before simulation. As a result, kMC has to rely on MD calculations to determine the possible transition events and their rates.

Based on the discussions, we can find that not a solo simulation method can model surface morphology under ion irradiations without taking results from other methods. The continuum method relies on MD simulations or Monte Carlo method to obtain quantitatively information of collision damages. The MD simulations cannot model slow processes that are crucial for the surface evolution. The kMC can model slow processes, but it needs knowledge from MD simulations to specify possible transitions
and their rates. As a result, a hybrid model seems to be the best choice for simulation of surface evolution under ion irradiation.

2.3 Existing atomistic models

As discussed in Section 1.2.2, the physical processes involved can be divided into two major categories, i.e., the prompt and gradual processes, by their different duration of time frame. For the prompt processes, the major task is to model the collision cascade. There are two major computational methods for such task, i.e., BCA-based (Binary Collision Approximation) Monte Carlo method and MD simulations. The BCA-based method treats the cascade as a succession of independent two body collisions, and simulates the random walk of particles in order to obtain the properties of the system statistically. It gives fast and reliable results for an overall picture of energy loss, damage geometry and ion range. In contrast to BCA models, MD simulations fully integrate the equation of motion for all atoms simultaneously. As a result,
MD simulations provide more reliable quantitative information of the whole collision process, but the price to pay is a much more intensive computational resource than for BCA codes [77]. The existing atomistic models for surface evolution are based on either Monte Carlo method or MD simulations.

2.3.1 Monte Carlo codes for ion-material interaction

For practical applications, people are only interested in certain physical parameters or an overall picture of the damage. In such case, the BCA-based Monte Carlo models have their advantages over MD simulations. The most widely used Monte Carlo code for ion-material interaction is the SRIM (the Stopping and Range of Ion in Matter) program [78] that is based on the former version TRIM [79] and TRIM.SP [80]. In these codes, the most important aspects and assumptions of the collision and energy loss process are as follows:

- The target is assumed to be amorphous;
- Only two atoms are evolved in each nuclear collision. The collision cascade are sufficiently diluted so that the target atoms can be assumed to be at rest prior to each collision;
- For each nuclear collision, the impact parameter and the species of the collision partner are determined from random numbers;
- The deflection angle of the binary collision is evaluated by the classic MAGIC routine
- Excitation or ionization of electrons only enters as a source of energy loss (i.e., the inelastic energy loss), but does not influence the collision dynamics;
- The potential for the nuclear collision is Moliere potential or the Kr-C potential for the early versions and the ZBL universal potential for later version;
• Use local or nonlocal free-electron-gas approximations for the electric energy loss (i.e., the inelastic energy loss)

• The planar surface model is employed as the sputtering criteria [41].

The SRIM program can calculate the radiation damage very fast. A typical SRIM calculation only takes a few minutes, which is much faster comparing to days or weeks needed for MD simulations. Thus, SRIM is usually used by researchers to quickly assess or estimate roughly irradiation damages, such as sputtering yield. The intrinsic limitation of SRIM code and other BCA-based codes is that BCA breaks down for low-energy regimes, at which the collisions are many-body collisions instead of two body.

SRIM is designed to deal with amorphous targets. However, most metals maintain crystalline structure under bombardments, leading to the failure of the assumption of amorphous state. Moreover, the stopping power is weaker in the crystalline directions, resulting in larger ion range if the ion travels in the crystalline directions. Such effect is called ion channeling. Thus, the atomic structure of the target material cannot be ignored if ion channeling exists in the system. This has been solved by the BCA-based Monte Carlo code MARLOWE developed by Robinson [81]. It is for computer simulation of atomic collision in crystalline solids.

SRIM and MARLOWE are only capable of static calculation of irradiation damage, since they consider each ion impact is independent from each other, ignoring any cumulative effects. This is a reasonably assumption for an elemental target irradiated by noble gases. But, if the target is a binary compound material, such as AuAg, then the composition profile of the target changes as irradiation due to preferential sputtering [82]. By realizing this problem, Moller and Eckstein developed the TRIDYN code (TRIM.SP DYNamical), which includes fluence dependent target changes and changes of local concentration distribution of multicomponent targets [83, 84]. The dynamic updates of the target surface is accomplished by slicing the target into small layers, whose composition is updated every a few impacts. Hou later on developed a
parallelized version, named as DYNAMIX (DYNamic transport of multi-Atom material MIXing), with another few new features such as detection of saturation state [85]. TRIDYN is also a good tool to investigate the interfaces of a multilayer films under ion irradiation.

2.3.2 Monte Carlo hybrid models for surface topography evolution

Most existing atomistic models for simulating surface evolution use Monte Carlo method to model ion-material interactions, similar to the codes introduced in the previous section, along with a proper model to account for surface diffusion. Cuerno et al [86] introduced a simple discrete stochastic model that used the local slope and the coordination number to determine the sputtering yield and the Hamiltonian energy to determine the diffusion process [87]. Later, this model was enhanced by Koponen et al [88, 89] by simulating the entire collision cascades based on BCA algorithm. They found that the ripples can form with and without diffusion, implying the presence of ion-induced surface diffusion mechanism proposed later by Makeev et al [14]. Even though it uses BCA to simulate collision cascade, Kopone’s model is only capable of simulating ripple formation within the BH linear regime. In order to investigate the non-linear regime, Cuerno’s model has been further extended to kinetic Monte Carlo simulations by Hartmann et al [57, 90–93], Chason et al [56, 94] and Stepanova et al [95]. In these models, the sputtering process is modeled by employing Sigmund’s sputtering theory [42], according to which the removal rate of a particle on the surface is proportional to the energy deposited there. The energy density deposited $E(x', y', z')$ at point $(x', y', z')$ is given by an Gaussian ellipsoid, with the local reference system defined as $z$-axis same as beam direction and $x$-$y$ plane perpendicular to the beam and origin set to the impact point, as already introduced in Eq. (1.5). In order to refer to it easily, the equation is rewritten here

$$E(x', y', z') = \frac{\epsilon}{(2\pi)^{3/2}\sigma \mu^2} \exp\left(-\frac{(z' + d)^2}{2\sigma^2} - \frac{x'^2 + y'^2}{2\mu^2}\right)$$

(2.1)
$d$ is the average ion penetration depth from the impact point. $\sigma$ and $\mu$ are the widths of the distribution parallel and perpendicular to the ion stopping points, respectively. $d$, $\sigma$ and $\mu$ can be calculated by SRIM code. $\epsilon$ is the energy of the ion. Figure 2.4 is a sketch showing the sputtering process and diffusion process. For each single-ion impact (left of Figure 2.4), the impact point is randomly chosen. Then the sputtering probability of its nearby surface atoms can be calculated according to Eq. (2.1). The kMC procedure is used to determine which atoms to be sputtered. Meanwhile, the surface atoms undergo diffusion (right of Figure 2.4) that is modeled by a few different models such as the net bond-breaking models [57]. The simulation results by these models show good agreement with the predictions of the nonlinear continuum theory for how the ripple evolution depends on the wave vector, defect kinetics, and ion-surface interaction [56]. This is not surprising since these kMC models are designed with the exact assumptions as linear BH theory. These models can also be performed on time scales where nonlinear effects become more important. Kinetic roughening is found for intermediate time. For longer time scale, the final surface patterns rely on the choice of surface diffusion model [90].

The kMC models are designed with the same assumptions as the continuum theories. On the one side, they can reproduce simulation results that are in very good agreement with the prediction of continuum theories. On the other hand, they also suffer the same drawbacks with the linear BH theory and its extensions.

Recently, an atomistic code named TRIDER (TRansport of Ions in matter with DEfect Relaxation) has been developed to simulate surface evolution, by modifying and enhancing the TRIDYN code [19,58]. The way of modeling ion transportation in the target material is kept as the same with TRIDYN, i.e., based on BCA algorithm. However, the way of modeling the target material is different. TRIDYN models the target as an amorphous material consisting with small layers. By contrast, TRIDER code treats the target as perfectly arranged discrete crystal lattices, which enables the code to simulate crystalline targets. Another major improvement is that the dynamics of the defects are simulated by kMC method. The simulation algorithm
Figure 2.4.: Sketch showing the sputtering process and diffusion process. The model consists of a square field of discrete height variables $h(x, y)$, corresponding to piles of $h(x, y)$ particles at position $(x, y)$. Left: each ion impact is modeled by a distribution describing the energy deposited by the ion. Atoms on the surface are removed with a probability proportional to the energy. Right: surface diffusion of atoms, by hopping to nearest neighbors with a probability determined by Arrhenius formula. (Figure taken from [90])

of the TRIDER code can be illustrated by Figure 2.5. TRIDER code mimics the real experiments, where ions collide the surface, leading to creation of vacancies and defects. These point defects then move around and interact with each other.

The simulations of silicon surfaces under Ar$^+$ irradiation using TRIDER code has succeeded in reproducing the phase diagram reported by Madi et al [47], with difference of a few degrees in the transition angles. By studying the morphology evolution with and without sputtering, it has found that defect kinetics is the dominating force for pattern formation for the angles smaller than 60°. It is in accordance with the predication of the recent developed continuum theory [43]. But for grazing angles (> 80°), erosion is driving force for pattern formation. This does not contradict with Norriss theory due to its failure to predict the transition of ripple orientations at high
angles [43]. Besides, coarsening of the surface structures is found for all energies of the ions.

The major Monte Carlo codes in the field of modeling surface morphology evolution by ion irradiation can be summarized by a diagram as shown in Figure 2.6. TRIM is the code that most of codes are based on. All codes have their own pros and cons. What we have learned is that the combing of different simulation methods to model complex systems has become a trend. A balance between accuracy and efficiency is crucial for the success of such hybrid models.
Figure 2.6.: A diagram showing the relationship and evolution of the MC models

### 2.3.3 MD-based hybrid models for surface topography evolution

The existing MD-based hybrid models for surface topography evolution are mainly MD/continuum multiscale models. In these models, MD simulations are used to obtain the average mass redistribution by single ion impact, characterized by a crater-shape surface response \([43, 54, 55, 69, 96]\). The use of the crater data is different in these models. Kalyanasundaram et al \([69]\) and Hossain et al \([55]\) incorporated the shape of the craters with a continuum theory and numerical integration was conducted to obtain resulting morphology. They found that the impact angle dependent mass redistribution is the underlying mechanism for ripple formation and orientation. The saturation of ripple amplitude is also observed, which is attributed to the asymmetry of the crater rim. Another model uses the moment form of the craters \([43, 54]\). An analytical equation is developed from first principle derivation in a form of the first moment of the craters. The advantage of the crater-moment based theory is that it
can predict the phase diagram just by calculating the moment of the crater. The limitation of the theory has been discussed in details in Section 1.3.1.
3. MODELING AND THEORY

The hybrid MD/kMC model developed in this work is differentiated from previous atomistic simulations \[56,57\] primarily by the use of the crater functions to treat ion impacts. This model uses craters obtained from MD simulations (using LAMMPS \[97\]) to consider the prompt mass redistribution due to single-ion impacts. Defect migration, which is missing in previous models using crater functions, is treated by a kMC Arrhenius model. In this chapter, each component of the model is discussed in details, followed by a brief description of the code implementation.

3.1 Model the target material

When a semiconductor material such as silicon is irradiated by ion beams, an amorphous layer with thickness about the same with the ion stopping range is found to form quickly at ion fluence as low as \(10^{14} \text{ cm}^{-2}\), which is too low for any possible surface patterns to emerge \[70\]. In light of this, most of models such as TRIM consider the target as amorphous with atoms at random locations for the whole bombardment including the beginning. However, the target is modeled in a different way here. The surface is considered to be an \(M\)-by-\(N\) grid with each grid coordinate containing the height of the surface relative to the initial height. The size of the grid is set to be the same as the average atomic spacing of the target atoms. The major reason for using such structure is to make it easy to incorporate with the crater data that are calculated by dividing the surface into grids. Another reason is to simplify surface diffusion for the sake of computer efficiency to avoid modeling of off-lattice diffusion.

A slab periodical condition is applied to the target, i.e., periodical conditions are used in lateral directions (\(x\) and \(y\) direction) but no periodical condition is used in the direction of ion beam (\(z\) direction). The initial surface is randomly rough with
amplitude of one atomic diameter (about 0.27 nm for silicon), as illustrated in Figure 3.1.

3.2 Simulation of single-ion impacts by landing craters

The model considers each ion impact to result in a crater, which is understood to describe the average change in the local surface due to a single impact. The typical method of obtaining such a crater is to use MD to simulate many (typically 500-2000) single impacts at a prescribed incidence angle on a flat surface. Taking the average result of each MD impact and averaging the height change at each point relative to the impact location leads to the crater. In general, a crater has lateral and longitudinal extent of a few nanometers, results in sub-Angstrom height changes over the affected area, and has a distinct pit and rim. Examples [98] can be seen in Figure 3.2.
Figure 3.2.: Examples of crater functions. In all plots, the black arrow indicates the ion beam direction and impact location. The key features are clearly visible, including (1) the presence of distinct craters and rims, (2) the increasing projection of the rim along the projected beam direction, and (3) the elongation of the crater at higher angles.
3.2.1 Ion generation, ion direction, impact point and shadowing effect

The bombardment process begins as soon as the initial surface is set up. Ions are considered to generate inside a plane that is a few nanometers above the initial surface (2 nm is used in this work). Then the ions progressively approach to the surface until they collide with the target at impact points. Here we explain how the impact point is calculated and how the shadowing effect is achieved.

Prior to the simulation proper, a 3D beam unit vector \( \vec{v}_{beam} \) is obtained based on the global angles of incidence and azimuth, \( \theta \) and \( \phi \) respectively.

\[
\vec{v}_{beam} = \sin \theta \sin \phi \hat{i} + \sin \theta \cos \phi \hat{j} - \cos \theta \hat{k}
\]  

(3.1)

Denote that the ion is generated at \( r_0 = (x_0, y_0, z_0) \). The ion will then march from the initial point to the surface along the direction of \( \vec{v}_{beam} \) by advancing a unit distance (we use 1 Å in the simulations) for each iteration, \( i.e., \)

\[
\vec{r}_{n+1} = \vec{r}_n + \vec{v}_{beam}, \ n = 0, 1, 2, ... 
\]  

(3.2)

until it intersects with the surface. Since this procedure mimics how ions approach a surface, the shadowing effect is implemented automatically.

3.2.2 Determination of the local slope and local incidence angle

Local slope

Slope is found as a 2D gradient vector giving average slope in the \( x \)- and \( y \)-directions, averaged over a square area. The generalized procedure is shown below; in the specific case, the function \( f(x, y) \) is the height of the surface at \( (x, y) \). Note that the unit is in the atomic spacing here. Figure 3.3 explains how to calculate \( M_x \) and \( M_y \), which is the \( x \) and \( y \) component of the local slope, respectively.
Figure 3.3: Sketch showing the calculation of local slope by averaging over a square area.
Thus, $M_x$ and $M_y$ are given by

\[
M_x = \frac{1}{n(n+1)} \sum_{i=0}^{n} M_{x=i} \quad (3.3a)
\]

\[
M_y = \frac{1}{n(n+1)} \sum_{j=0}^{n} M_{y=j} \quad (3.3b)
\]

Finally, the local slope $\nabla$ can written as

\[
\nabla = \langle M_x, M_y \rangle \quad (3.4)
\]

Note that here, the divisor in the average slope calculation is $n(n+1)$. This is because it is faster computationally to divide by the length of the slope interval ($n$) after the summation rather than before. The $(n+1)$ term is of course the total number of slopes from which an average is obtained.

In the actual program, the area used in the above procedure is defined by the parameter GRAD_EXTENT which gives the extent of that area in the $\pm x/y$ directions. Therefore, $n = 2 \times$ GRAD_EXTENT; other steps of the procedure are essentially the same. The parameter GRAD_EXTENT is determined by the lateral size of collision cascade. In most simulations, we use GRAD_EXTENT=5. In other words, the local slope is calculated based on a square area of size about 2.5 nm by 2.5 nm.

**Local incidence angle**

We define a normal vector with respect to the local surface, $\vec{n} = M_x \vec{i} + M_y \vec{j} - \vec{k}$, and obtain the unit vector $\vec{e}_n$ from $\vec{n}$. The local angle of incidence is defined by:

\[
\theta_i = \cos^{-1}(\vec{e}_n \cdot \vec{v}_{beam}) \quad (3.5)
\]

The vector tangent to the projected beam trajectory along the pseudoplane defined by $\nabla$ is found as $\vec{e}_t$, i.e., the unit vector of $\vec{t}$, where

\[
\vec{t} = \vec{v}_{beam} - \cos \theta_i \ast \vec{n} \quad (3.6)
\]
3.2.3 kinetic Monte Carlo treatment of surface diffusion

In the present simulation, surface diffusion is treated discretely using an Arrhenius rate law in a manner similar to that of [56, 57]. The relative probability for an atom on the surface to undergo a diffusion event is given by the Arrhenius equation:

$$v = \left(\frac{2k_BT}{h}\right)\exp\left(-\frac{\Delta E}{k_BT}\right)$$  \hspace{1cm} (3.7)

Here, $T$ is the surface temperature, which is treated as a constant value over the entire surface and is taken as input. $k_B$ and $h$ are the Boltzmann and Planck constants, respectively. The principal variable under consideration here is the activation energy, $\Delta E$, required to cause a hop.

There are several methods to determine the activation energy. A widely-used one is the net-bond difference (NBD) method [56, 57], which incorporates the net change in fulfilled bonds between the initial and final positions of a possible hop. The NBD method breaks down the activation energy into three components, given as:

$$\Delta E = E_s + E_{nn} + E_{ES}$$  \hspace{1cm} (3.8)

Here, $E_s$ is a substrate energy barrier present for all hops. $E_{nn}$ is the net bond-breaking energy, based on the initial and final number of nearest neighbors for the given hop, such that

$$E_{nn} = \begin{cases} 0 & \text{if } nn_i \leq nn_f \\ E_b(nn_i - nn_f) & \text{if } nn_i > nn_f \end{cases}$$  \hspace{1cm} (3.9)

Here, $E_b$ is the neighbor bonding energy. Finally, the Ehrlich-Schwoebel barrier energy, $E_{ES}$, represents an additional energy barrier which applies only to hops which approach a step edge on the surface, but does not apply to atoms already on a step edge. The ES barrier is shown schematically in Figure 3.4. The ES barrier inhibits atom diffusion over step edges, resulting in surface instability. However, step structures only exists on crystalline surfaces. On an amorphous surface, steps are almost nonexistent and so ES barriers are not considered in this work.
Figure 3.4.: Graphic showing hops with and without Ehrlich-Schwoebel barriers. For the atom at position ‘A’, no barriers are present because the atom is already at a step edge. For the atom at position ‘B’, a hop to the left is allowed since no step edge is present, but a hop to the right is inhibited by the presence of an ES barrier.
The second method is derived from the curvature-based Mullins diffusion model [99], where the chemical potential of a point on the surface is given in terms of the curvature $\kappa$:

$$\mu(\kappa) = \kappa \gamma \Omega$$  \hspace{1cm} (3.10)

where $\Omega$ is the atomic volume, and $\gamma$ is the surface free energy. In simulation the surface free energy $\gamma$ is converted in terms of the lattice length and the atomic volume $\Omega$ is considered as unity ($a^3 = 1$). The curvature is given as the sum of the curvatures in the $x$- and $y$-directions:

$$\kappa = a^{-2}[h(x + a, y) + h(x - a, y) + h(x, y + a) + h(x, y - a) - 4h(x, y)]$$  \hspace{1cm} (3.11)

The resulting activation energy for a hop is then

$$E_a = E_s + \Delta \mu_{ij}$$  \hspace{1cm} (3.12)

Note that if the $j_{th}$ site is more stable than the $i_{th}$ site in this model, the activation energy can be less than the supposed barrier energy. Aside from the barrier term, this model of the activation energy is identical to that given by Siegert and Plischke [87], although the term “Hamiltonian” is used as they employ a different formalism.

The third method considers the direction of each bond to determine the activation energy associated with a hop, and some of the concepts of this model are shown in Figure 3.5. To begin with, each surface atom can have two main types of bond-breaking behavior: first, a bond can be completely severed before a corresponding bond is formed (if one exists). Second, if a bonding atom for the initial site is a neighbor of a bonding atom for the ending site, the new bond will be able to pull the hopping atom away once the hopping atom is equidistant from both points, and thus the energy required to make this hop is less than that required to fully break a bond. While this pulling effect can apply for any correlated pair of bonds at the initial and final sites, in this model only adjacent bonding atoms are considered, as for atoms further away from each other (e.g. those bookending a hop) the effect is small and the energy barrier is nearly the bond energy. Adjacent bonds are present in adatom hops over a flat surface as well as in edge hopping.
Figure 3.5.: Representative diagram of different bond types that may be encountered in a hop. The green ‘X’s represent adjacent bonds which contribute an energy barrier which is less than the bond-breaking energy, while the red ‘X’s show bonds which are completely broken before the hop is complete. Sketch (a) shows motion between two equal-height locations, i.e. a hop along a “flat” surface, while (b) indicates hops between locations of uneven heights, showing that there are no adjacent bonds in such an event.
In this treatment, the energy barrier for a hop is based on the types of bonds present as well as the height difference between the initial and final sites. The possible bond configurations in this treatment are as follows:

- **Flat surface hop** \((h_i = h_j)\): As seen in Figure 3.5(a), there exists a minimum energy barrier due to the adjacent surface bonds, which is equivalent to the activation energy for an adatom hop of 0.69 eV reported in [100]. The end atoms are those which border the initial and final sites along the line of action, and contribute a barrier equal to the full bond energy of 1.65 eV, also given in [100]. Bonds which border each site perpendicularly to the line of action are labeled as “wall” bonds. A wall atom at the initial site contributes the lower energy barrier if it can be canceled by a wall atom at the final site (this configuration is identical to that of the surface atoms seen in Figure 3.5(a), simply in the horizontal rather than vertical dimension); otherwise it must be completely broken and contributes the higher energy barrier.

- **Downward hop** \((h_i > h_j)\): This case is the reverse of that seen in Figure 3.5(b). As no adjacent bonds are possible, only bonds at the initial site are considered, and all contribute the full bond-breaking energy barrier. However, there is no contribution from the surface bond at the initial site, as the hopping atom is considered to remain attached to this atom before, during, and after the event.

- **Upward hop** \((h_i < h_j)\): This is identical to the downward hop case with one exception: the surface bond contributes a full bond-breaking energy barrier to the activation energy, as it is broken completely. However, the final site, which borders the hopping atom in its initial configuration, contributes no barrier as once again the atom “roll” along this bond. This case is identical to that of Figure 3.5(b). Because of the additional energy barrier to break the surface bond, upward hops are less likely than downward hops; this implies a downward current of diffusing atoms.
Noting that in this formulation of activation energy the bond energy must be less than the surface hop energy barrier, \( E_s \), the above energies are given by:

**(flat)**

\[
E_a = E_s(n_{w,i} + 1) + (E_b - E_s)[\max?(n_{w,i} - n_{w,j}, 0)] + E_{n_{e,i}} \quad (3.13)
\]

**(down)**

\[
E_a = E_b n_i \quad (3.14)
\]

**(up)**

\[
E_a = E_b (n_i + 1) \quad (3.15)
\]

As a final note, the magnitude of height changes due to hops up or down is not considered; in theory this would increase the energy barrier for a hop even further, but treating this would become rather complicated as a myriad of configurations would be possible.

All the simulations in this work used the net-bond difference (NBD) method to calculate activation energy. The other two methods were tested in attempt to improve the atomistic diffusion approach. However, in general, the other two methods were found to perform no better than the simple net-bond difference model.

### 3.3 Overview of the code implementation

#### 3.3.1 Flow charts

The surface is considered to be an M-by-N grid with each grid coordinate containing the height of the surface relative to the initial height. The surface is initially randomly rough with amplitude of one atomic diameter (about 0.27 nm for silicon). Following initialization, each pass through the main loop simulates a single ion impact, followed by one or more diffusion events depending on the post-impact surface configuration. Output is produced at regular intervals with frequency given as an input, consisting of a complete snapshot of the surface containing a summary of the simulation parameters, a brief statistical overview, and the height of each coordinate.
Figure 3.6.: Top-level flow diagram of the simulation. Solid arrows indicate program flow, whereas dotted lines denote data flow of the surface grid. A simplified flowchart showing the top-level code structure is shown in Figure 3.6, 3.7, and 3.8.

3.3.2 Interface between impact and diffusion components

The interface between impact and diffusion components consists of two parts. At the highest execution level, two “clocks” are used to track simulation time, as illustrated in Figure 3.9. Ion impacts are tracked by one clock, and are assumed to have a uniform time interval between each event which is based on the input value for the ion flux. Diffusion events do not occur at a constant rate, so the sum time taken by all diffusion events is tracked separately and compared to the total impact time to determine when events should occur.
Figure 3.7.: Flow chart for crater function (CF) loop
Figure 3.8.: Flow chart for diffusion loop
On a lower level, diffusion hop rates are continually updated throughout the simulation. Anytime a coordinates height is changed by diffusion, the surrounding grid points are checked for changes in their hopping rates. Similarly, after an impact the points affected by the crater function (within a certain cutoff range, typically equivalent to a 1% change in height) are also checked for changes in diffusion rates. To allow this process to occur without excessive runtime, each hop is treated as a data structure and the hops are stored in “bins” corresponding to each possible surface configuration with pre-calculated hopping rates.
4. CRATER FUNCTIONS

The crater functions are a part of the input for the hybrid model. The quality of the crater functions directly affects the resulting morphology. Thus, to establish a reliable way to obtain the crater data is crucial. This chapter focuses on the details of the MD simulations to obtain crater functions, including selection of the interatomic potential, generation of amorphous silicon, multiple single-ion impacts and data analysis. LAMMPS [97] code is selected to perform the MD simulations due to its broad choice of interatomic potentials, fast performance on multiple cores and high flexibility of customized features.

4.1 Methods

4.1.1 Selection of the interatomic potential

The reliability of MD simulations relies primarily on the quality of the interatomic potential employed in the simulations. Usually, most of the potentials are fitted to experimental results or ab initio calculations to reproduce the properties of the modeled material, such as its structural, elastic or thermal properties. The ion-material interaction is a complex process. As a result, in order to well simulate ion-material interactions, a good potential should at least meet the following requirements [101].

Firstly, the potential should be able to describe well the crystalline, amorphous and liquid states, since all the three phases are present in ion-material interactions. Secondly, the potential should predict the correct temperatures for phase transitions. If not, there will be issues for the development (i.e. solid-to-liquid phase transition) and the termination (i.e. liquid-to-solid phase transition) of collision cascades. Thirdly, binding of atoms at surface should be modeled correctly. Atoms at surface are bonded
differently than in bulk due to reduction of coordination numbers. Most of the potentials are developed in the scope of bulk properties. They may not work well for surfaces and interfaces. If the surface binding is too weak, the surface will collapse under ion bombardment, leading to no formation of craters. On the other hand, if the surface binding is too strong, this will directly affect the hole formation of a crater since atoms need more energy to escape the surface binding barrier. Also, the shape of the crater rim that is caused by mass redistribution across the surface is suppressed due to stronger binding.

There are a few potentials widely used to model silicon, including the Stillinger-Weber (SW) potential [102], the Tersoff potential [103–105] and the environment-dependent interatomic potential (EDIP) [106]. All of these potentials can be expressed as a sum of two terms, one for two-body interactions and another for three-body interactions.

\[ E = \sum_{i<j} V_2(r_{ij}) + \sum_{i<j<k} V_3(r_i, r_j, r_k) \] (4.1)

In SW potential (shown in Eq. 4.2), the two-body term \( \phi \) consists of both attractive and repulsive interactions between a pair of atoms. The three-body term represents the weakening of bonds.

\[ E = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_{ijk} g(r_{ij})g(r_{ik}) \left( \cos \theta_{ijk} + \frac{1}{3} \right)^2 \] (4.2)

Where the \( g(r) \) is a decaying function and \( \cos \theta_{ijk} \) is the angle formed by the \( ij \) bond and the \( ik \) bond.

The Tersoff potential is essentially different from the SW potential for its use of bond order (shown in Eq. 4.3). Its two-body part \( \phi_R \) is merely the repulsive pair interaction. The three-body part describes the attractive energy that depends on the local environment, characterized by the Pauling bond order \( p(\xi) \).

\[ E_i = \sum_{ij} [\phi_R(R_{ij}) + p(\xi_{ij})\phi_A(R_{ij})] \] (4.3)

The EDIP potential is inspired from the SW potentials. It is expressed as the sum of a pair bonding term and an angular term similar to the SW potential. But
both terms also depend on the local coordination number \( Z_i \), which is similar to the concept of bond order, as shown in Eq. (4.4).

\[
E_i = \sum_j V_2(R_{ij}, Z_i) + \sum_{jk} V_3(R_{ij}, R_{jk}, Z_i)
\]  (4.4)

Each of the potentials has its own advantages and disadvantages \([101, 107, 108]\). The SW potential has been shown to accurately reproduce the elastic properties and the correct melting temperature \([102]\), but it is not good for amorphous state \([109]\). The Tersoff potential is a very good description for crystalline silicon, however it overestimates greatly the melting temperature \([107]\). The EDIP potential models the crystalline, amorphous and liquid states fairly well, but it underestimates the melting temperature by 20% and there are some unphysical behaviors for liquid phase \([101]\). Thus, there is no potential that can outperform others. It is agreed that not a single potential can fully describe the properties of silicon under different phases.

Another difficulty of choosing proper potential is that there is no available crater data from experiments to test the potentials. Samela et al performed MD studies to compare the crater shapes obtained by these potentials and their modified versions \([101]\). Although it was found that the crater shape varied with the potentials, it is hard to conclude which potential is the best choice for obtaining crater data.

In this study, the SW potential is employed to model interactions between silicon atoms since it has been tested in many MD simulations of ion bombardment and its reliability has been confirmed \([65, 70, 110–112]\). The parameters are slightly different from the original set. The parameters \( \epsilon \) and \( \lambda \) are scaled by factors of 1.5 and 0.76, respectively, to better represent amorphous phase \([109]\). The complete set of parameters of the modified SW potential can be found in \([109]\).

The ion-silicon interactions are modeled by the ZBL universal potential proposed by Ziegler, Biersack and Littmark \([113]\) in the form of

\[
V(r) = 14.4 \frac{Z_1 Z_2}{r} \phi(r) \ (eV)
\]  (4.5)
where $Z_1$ and $Z_2$ are the atomic numbers of the atom pair, $r$ is the interatomic distance in unit of angstrom, and $\phi(r)$ is the non-dimensional screening function, given by:

$$\phi(r) = \sum_{i=1,4} A_i \exp \left( -\frac{b_i r}{a_u} \right)$$  \hspace{1cm} (4.6)

$A_i$ and $b_i$ are predefined parameters listed in Table 4.1. $a_u$ is the reduced radius given by:

$$a_u = \frac{0.8854}{\frac{Z_1^0}{23} + \frac{Z_2^0}{23}} a_{Bohr}$$  \hspace{1cm} (4.7)

where $a_{Bohr}$ is the Bohr radius is 0.529 Å.

<table>
<thead>
<tr>
<th></th>
<th>$i = 1$</th>
<th>$i = 2$</th>
<th>$i = 3$</th>
<th>$i = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>0.1818</td>
<td>0.5099</td>
<td>0.2802</td>
<td>0.02817</td>
</tr>
<tr>
<td>$b_i$</td>
<td>3.2</td>
<td>0.9432</td>
<td>0.4029</td>
<td>0.2016</td>
</tr>
</tbody>
</table>

For high energy collisions (> 10 keV), some silicon atoms can also come very close to each other, leading to the penetration of the shells of atoms. In this case, the ZBL potential is also used for silicon-silicon interactions at close separation to bring the repulsion at very small distance.

4.1.2 Preparation of the amorphous target

The amorphous silicon (a-Si) used in this work is prepared by the melting-quenching method in which a crystalline silicon (c-Si) is melted and then quenched rapidly in a MD simulation [114–116]. Here, the procedure is presented as follows.

1. A crystalline silicon consisting of $15 \times 10 \times 10$ lattices is created, resulting in a target with dimensions of $81.15\text{Å} \times 54.31\text{Å} \times 54.31\text{Å}$ containing 12000 atoms. With this size, the target can enclose properly the whole collision cascades produced by < 1 keV Ar$^+$ bombardment.
2. Periodical boundary conditions (PBC) are applied to all three directions. The target is heated up to 4000 K by velocity scaling. After kept at 4000 K for 15 ps, the target is cooled down to 1K by a cooling rate of $3.33 \times 10^{13} \text{ K/s}$. Another 15 ps is used to further equilibrate the target. The target is considered as an NVT ensemble and the time step is set to 0.5 fs.

3. After complete step 2, a bulk a-Si target is created. This bulk a-Si target is then modified to become a surface by using a slab PBC configuration, i.e., PBC applied for the lateral directions (parallel to the surface, denoted as $x$ and $y$ axes) and no boundary condition in the direction of ions (normal to the surface, denoted as $z$ axis). The bottom 5 Å of atoms are held fixed to prevent the target from moving. Due to the change of PBC and the creation of a surface, the target is no longer in the equilibrium state. To bring the target back to the stable state, the target is kept at 1K using NVT integration until the potential energy ceases to increase.

The melting-quenching method is not the only available method for preparation of amorphous targets. The WWW method [117] is another main method that obtains $a$-Si by repeatedly rearrangement of bonds with the preservation of the tetrahedral structures using Monte Carlo scheme. Both methods have its own advantages and disadvantages. The WWW method is considered to be one of the best method for generating good quality of amorphous targets that is homogeneous and continuous [118]. The major disadvantage of the melting-quenching method is that it relies on the ability of the potential to realistically model the liquid phase since the target is melted during the preparation [108]. However, Biswas et al has shown that the quality of the amorphous structures generated by melting-quenching method is comparable to the WWW method [114]. Furthermore, the WWW method is very computational demanding [43,108,118]. As a result, it is almost impossible to optimize large structures. Methods such as combination of small optimized blocks have to be used in order to obtain large structures [118]. On the contrast, the melting-quenching method is
For example, even for a system as small as 216 atoms, the WWW method required at least an order of magnitude more computer time, not to mention a large system with more than $10^4$ atoms as used in this work.

### 4.1.3 MD Simulations of single-ion impacts

For each ion impact, the a-Si target is configured as shown in Figure 4.1. The slab boundary conditions are used. The bottom 5 Å of the target is fixed to prevent the target from moving downwards under ion impacts. A layer with thickness of 1 nm is used as a thermostat layer that removes kinetic energies using Berendsen thermostat [119] to keep the target temperature constantly at 1K. The thermostat layer is served as a heat sink that mimics the bulk material. The free layer contains all the rest of atoms above the thermostat layer. No thermostat is applied to the free layer. Atoms in the free layer are considered as a NVE ensemble. For each impact run, an ion is generated randomly above the surface with a direction determined by the incidence angle and the azimuthal angle. The time step is chosen to be 0.1 fs to correctly simulate collisions between the high-velocity ion and target atoms. The collision cascade is allowed to fully develop for 11.4 ps. The whole target is then cooled down to 1K to freeze the radiation damage for crater function calculation.

In order to investigate the effect of ion energy on surface evolution, simulations of Ar$^+$ ions with various energies (100, 250, 500, 700 and 1000 eV) on the a-Si target were performed. For each energy, 1000 or 2000 ion impacts were simulated at incidence angle from 0° to 85° with 5° increments to achieve good statistics. Furthermore, simulations of ion species Xe$^+$ and Kr$^+$ with 1000 eV impact energy were also performed to study the effect of ion masses.
Figure 4.1.: Configuration of the target for ion impacts. The target is configured with three different regions: (a) fixed layer to prevent the downward movement of the target, (b) thermostat layer to remove kinetic energies to avoid the overheating of the free layer, and (c) the free layer where the atoms are treated as an NVE ensemble.
Figure 4.2.: Cross-sectional view of the a-Si. There are no large voids and the defects are distributed homogeneously.

4.2 Results and discussions

4.2.1 Characterization of a-Si

The a-Si target prepared by the melting-quenching method using SW potential must be characterized first to ensure that it is a realistic continuous random network. Particularly, the structure should be dense enough, free of large voids, and uniform in terms of defect distributions in order to obtain reliable crater functions. The volume of the a-Si target remains almost constant during the preparation process. After careful calculation, it shows that the density of the a-Si target is about 3% less than c-Si, which is in good agreement with experiments [120]. Figure 4.2 shows a cross-sectional view of the a-Si slice with thickness of 5 Å. It is clear that there is no large voids and the defects are distributed homogeneously.

Table 4.2 lists the distribution of coordination numbers calculated with a cutoff radius of 2.8 Å. The average coordination number is 4.003, which is almost identical to crystalline silicon. The majority of the atoms (94.4%) have four neighbors. Only 5.6% of atoms have three or five neighbors, which is a sign of low density of voids and low internal stress.
Table 4.2: Distribution of coordination numbers

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>2.6%</td>
<td>94.4%</td>
<td>3.0%</td>
</tr>
</tbody>
</table>

The radial distribution function (RDF), or the pair correlation function, is an important structural characteristic that can be a very useful tool to examine the topology of an amorphous network, as it contains information such as the characteristic distances associated with different neighbor pairs [121]. In Figure 4.3, the RDF of the a-Si sample is compared with experimental results reported by Laaziri et al [121, 122]. There are two main differences between them. The maximum of the first peak is about 15% higher than the experimental RDF. Additionally, there is a small shoulder on the left of the second peak. Except these differences, the overall agreement is quite good, such as the peak positions and maxima.

To conclude, the density and the structure of the a-Si sample obtained by melting-quenching method have been examined by comparing its mass density, defect density, coordination number and RDF with experimental observations. The agreement is pretty good in general, which implies that the a-Si sample can be used in practice for MD simulations of ion impacts. Its reliability can further confirmed by the study of sputtering yield and crater functions in the next sections.

### 4.2.2 Sputtering yields and energy distribution of sputtered atoms

Sputtering has been considered as the driving force for surface evolution in linear BH theory and its extensions for the last decades. The realization of the mass redistribution or crater functions has overturned this traditional view. Although the crater function theory asserts that sputtering is a negligible effect for surface morphology evolution at low and intermediate angles [43], the role of sputtering at glancing angles is still uncertain. Thus, the study of sputtering is of importance to elucidate
Figure 4.3.: Comparison of the RDF of the sample obtained by melting-quenching MD method with experimental result. The experimental data is taken from [109, 121, 122].
this problem. Furthermore, unlike the crater function, the sputtering yield can be measured in experiments and is available in literature. Thus, the sputtering yield obtained by MD simulations can be compared with available experimental data, which can be a way to verify the reliability of the MD simulations.

Figure 4.4 shows the sputtering yield of Si target as a function of Ar+ incident energy between 100 and 1000 eV at normal impacts. The MD simulation results are compared with TRIM computer simulation and experimental results by Wittmaack [123]. The MD results agree very well with the experimental results. On the other hand, the TRIM simulation results underestimate the sputtering results by about 15-25%.

The dependence of sputtering yield on ion energy can be well described by Sigmund’s sputtering theory [42] with the correction by Bohdansky [124] accounting for low-energy projectile [123]. According to the Sigmund sputtering theory, the sputtering yield of amorphous or polycrystalline targets for normal incidence can be given by

\[ Y(E) = \Lambda F_D(E) \]  
\[ \Lambda = \frac{0.042}{U_0} \]

with

\[ F_D(E) = \alpha S_n(E) \]

where \( E \) is the energy of incidence ion, \( U_0 \) the surface binding energy, \( S_n(E) \) the nuclear stopping power and \( \alpha \) the proportion of energy deposited on the surface. This analytical form has been found to predict sputtering yield with good agreement with experimental observations for high energy regimes [42,124]. However, at low energy regime, the predicted sputtering yield is largely overestimated due to threshold effects at surface [124]. Bohdansky proposed a correction term for \( S_n(E) \) to account for “effectively deposited energy” [124], as given by

\[ S_n^{\text{eff}}(E) = S_n(E) \left[ 1 - \left( \frac{E_{th}}{E} \right)^{2/3} \right] \left[ 1 - \left( \frac{E_{th}}{E} \right)^2 \right] \]
Figure 4.4.: Sputtering yield of Si target as a function of Ar$^+$ incident energy. The red dots represent the MD simulation results. The black squares are results obtained by TRIM calculation. The blue triangles are the experimental results from Wittmaack [123]. The line is intended only to guide the eye.
Figure 4.5.: The sputtering yield of Si target bombarded by three different ion species (Ar, Kr and Xe) of the same energy (1 keV) at normal incidence. The experimental results are from [125]. The lines are drawn to guide the eye.

where $E_{th}$ represents the threshold energy and depends on the energy of the ion, and the mass ratio of ion to target atom.

Figure 4.5 displays the effect of ion mass on the sputtering yield. The Si target is bombarded by three different ion species (Ar, Kr and Xe) of the same energy 1 keV at normal incidence. The experimental results are taken from Zalm [125]. There are no apparent dependence of sputtering yield on ion mass. This observation can be further confirmed by the additional experimental data reported by Zalm [125], as shown in Figure 4.6. These data represent the sputtering yield for ion energies of 200 eV, 500 eV, 1 keV and 2.5 keV. It is clear that the sputtering yield can either increase or decrease with ion mass.
Figure 4.6.: Experimental sputtering yield of Si target for Ar, Kr and Xe at energies of 200 eV, 500 eV, 1 keV and 2.5 keV. (Data are from [125])
Figure 4.7.: Angular distribution of sputtering yield for 500 eV Ar bombardment of Si. The experimental results are from [19,126].

In Figure 4.7, the angular distribution of sputtering yield for 500 eV Ar$^+$ bombardment of Si is displayed. Again, the MD simulations results are compared with TRIM simulation and experiments [19,126]. The MD results are in good agreement with the experiments at low angles ($<35^\circ$), about 30% higher than experiments at intermediate angles (between 35$^\circ$ and 75$^\circ$), and lower than the experimental data at glancing angles ($>75^\circ$). The sputtering yield reaches to maximum at angle about 68$^\circ$ for both MD and experimental results. The peak position predicted by TRIM is off by about 10$^\circ$. The MD simulation differs greatly with experimental data and TRIM simulation at glancing angles. This is probably due to very high ion backscattered rate. For example, 96% of incidence ions get backscattered at 80$^\circ$ in MD simulation, comparing with 57% for TRIM simulation. This leads to only small proportion of energies depositing in the target and eventually results in low sputtering yield.
Table 4.3: Statistics of the energy of the sputtered atoms for 500 eV Ar\(^+\) on Si at normal incidence. All in unit of eV.

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Minimum</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRIM</td>
<td>10.33</td>
<td>14.12</td>
<td>0.0124</td>
<td>5.68</td>
<td>157.12</td>
</tr>
<tr>
<td>MD</td>
<td>9.65</td>
<td>9.56</td>
<td>0.145</td>
<td>6.73</td>
<td>74.08</td>
</tr>
</tbody>
</table>

The energy spectrum of the sputtered atoms is very important for modeling the redeposition effect. When an sputtered atom leaves the surface, it may leave the surface permanently. However, if there are tall structures on the way of the sputtered atom, the atom may strikes the surface again. Thus, the redeposition effect can not be negligible, sometimes of importance, for morphology evolution at late stage when tall or steep structures are developed. Table 4.3 lists the statistical analysis of the energies of the sputtered atoms for both TRIM and MD simulations of 500 eV Ar\(^+\) on Si at normal incidence. The mean and median energies are similar, which indicates that the average energy taken away from the collision cascade by the sputtered atoms is about the same for both simulations. The maximum energy predicted by TRIM simulation is about twice larger than the one by MD simulation. However, there are only few than 0.5\% of sputtered atoms with energy higher than 74 eV. Thus, the two simulations can be seen to give about the same energy range of the sputtered atoms.

Figure 4.8 illustrates the energy distribution of sputtered atoms for both TRIM and MD calculations. The distributions are fitted to the theoretical form derived by Thompson [41] in which the energy spectrum can be expressed as Equation (4.12) for amorphous or polycrystalline targets.

\[
f(E) \propto \frac{E}{(E + E_{sb})^n} \tag{4.12}
\]

where \(n\) is a power factor with value about 3 and \(E_{sb}\) is the surface binding energy, which is usually considered to be equal to the heat sublimation. If \(n = 3\), it is easy to find that \(f(E)\) has a maximum value locating at \(E = E_{sb}/2\). This means that
the most probable energy is much lower than the mean energy. Thus, the energy spectrum can be used to estimate the approximate surface binding energy. By fitting to Equation (4.12), the surface binding energy has been predicted to be 3.4 eV and 5.2 eV for TRIM and MD simulations, respectively. By comparison, the heat sublimation of silicon is 4.7 eV that is different than the values predicted by both simulations. Thus, the fitting parameters can only be used for rough estimation.

### 4.2.3 Obtain crater functions

The crater function \( \Delta h(x, y) \) describes the average surface height change before and after an ion impact. In order to calculate the height change, the surface profile has to be obtained for surfaces before and after an ion impact. There are a few approaches to compute the surface profile. Kalyanasundaram et al [68] proposed a “probe-atom” method, in which a virtual single-atom probe was lowered to the surface and the surface height was defined as being a position where the interatomic force was below some threshold. The major problem for this method is that it overestimates the size of hills and underestimates that of valleys [54]. Norris et al [43] and Hossain et al [127] used an approach that tracks the changes in number of atoms in a two dimensional array of vertical columns that are decomposed from the surface. The change in number can be then transformed into height through atomic volume. This approach eliminates the problem of upward displacement of the surface that is caused by a stress wave reflection. However, it assumes the density of the surface is constant during ion impacts, which ignores the point defects generated by the ion.

Alternatively, the method proposed by Moseler et al [52] is employed in this study. After each impact, the target is divided into a two-dimensional (2D) array of small vertical columns with a cross section of 2.71 Å \( \times \) 2.71 Å. In such way, the surface profile is discretized into a 2D mesh with each cell of 2.71 Å \( \times \) 2.71 Å. The height of each cell is determined by the highest atom in the corresponding column.
Figure 4.8.: Energy spectrum of the sputtered atoms for 500 eV Ar+ on Si at normal incidence for (a) TRIM calculation, and (b) MD simulation. The red lines are the fitted curved to the analytical form as given by Equation (4.12).
Several sample craters are shown in Figure 4.9 for 500 eV Ar$^+$ on Si at various angles. The craters are of sub-angstrom in height. The key features are the central pit and the surrounding rim. The craters are symmetrical along the direction of the beam. At normal incidence, the crater is also symmetrical in the direction perpendicular to the beam. As incidence angle increases, the crater becomes more and more asymmetrical. The depth of the pit increases with increasing incidence angle up to 70° and then decrease with increasing angle. The pit is seen to elongate along the projected ion path as the impact angle increases. The rim is shown to maintain a largely consistent shape, but the center of the rim projects further along the projected ion path with increasing incidence angle.

4.2.4 Empirical analytical form of the crater function

Obtaining crater functions requires a significant amount of computational time to conduct MD simulations. To obtain good statistics, hundreds or thousands of
Simulations have to be performed. Thus, it would be valuable if researchers are able to share crater functions with each other. The question is what format should be used. It is almost impossible to publish the crater functions in a format of matrix as used in this work. Alternatively, Kalyanasundaram et al suggested to fit the discrete crater functions to an analytical form originated from Davidovitch [128]. A crater is considered to be a modified difference-of-Gaussians as shown in Equation (4.13).

\[
\Delta h(x, y) = h_1 - h_2 \\
= A_1 \exp \left(-B_1[D_1 x^2 + (y - C_1)^2]\right) - A_2 \exp \left(-B_2[D_2 x^2 + (y - C_2)^2]\right)
\]

A brief analysis of Eq. (4.13) will show that the first term represents the crater “rim” of redistributed material, while the second term describes the initial crater caused by the impact. Figure 4.10 illustrates the meaning of each parameter in the equation. \(A_1\) and \(A_2\) represents the amplitude of each Gaussian. \(B_1\) and \(B_2\) are related to the full width at half maximum (FWHM). \(C_1\) and \(C_2\) are the offset of the Gaussians from the origin. \(D_1\) and \(D_2\) determines the elongation of the Gaussians. Furthermore, the integral of \(\Delta h(x, y)\) can be taken over the surface to obtain the angle-dependent sputtering yield of a single-ion impact (neglecting density effects); as the function is essentially a difference-of-Gaussians the yield is simply

\[
Y(\theta)\Omega = \pi \left( \frac{A_1}{B_1\sqrt{D_1}} - \frac{A_2}{B_2\sqrt{D_2}} \right)
\]

where \(\Omega\) is the atomic volume.

There are two main benefits of using an analytical form. First, it can eliminate possible noise. The crater functions are the average from limited number of single-ion impacts. Theoretically, the noise could be lowered to unnoticeable level if a significant large number of impacts are performed. However, this would require too much computational time. On the other hand, the analytical form can smoothen out possible noise that is caused by limited number of ion impacts. Secondly, it becomes possible to publish crater functions in literature so that other researchers can reuse the data or make comparisons with their own data. For example, Table 4.4
Figure 4.10.: Sketch showing the difference of two Gaussian functions. $h_1$ and $h_2$ are the positive and negative Gaussian, respectively. $h_y$ is the sum of $h_1$ and $h_2$. $A_1$ and $A_2$ represents the amplitude of each Gaussian. $C_1$ and $C_2$ are the offset of the Gaussians from the origin. And $B_i = 1/(\sigma_i^2)$, $i = 1, 2$. (Image taken from [19])
Table 4.4: Fitting parameters of the analytical form for 500 eV Ar\textsuperscript{+} at normal incidence

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>B1</th>
<th>C1</th>
<th>D1</th>
<th>A2</th>
<th>B2</th>
<th>C2</th>
<th>D2</th>
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<tr>
<td>This work</td>
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<td>0.00643</td>
<td>0.0</td>
<td>1.0</td>
<td>0.995</td>
<td>0.0538</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[19]</td>
<td>0.134</td>
<td>0.0022</td>
<td>0.0</td>
<td>1.0</td>
<td>0.251</td>
<td>0.033</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[69]</td>
<td>0.205</td>
<td>0.00553</td>
<td>0.0</td>
<td>1.0</td>
<td>0.805</td>
<td>0.0315</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

provides an example of the fitting parameters for 500 eV Ar\textsuperscript{+} at normal incidence from different sources. The $D$ parameters are all zero due to the symmetry in both $x$ and $y$ direction. The $C$ parameters are all set to 1 since the pits are not elongated in the $x$ direction. The difference of $A_1$ and $A_2$ gives the depth of the pit. By analysis of the parameters, it can be observed that the crater function reported by Kalyanasundaram et al [69] is similar with this work in terms of pit depth and rim height. The crater reported by [19] is shallower in the pit and shorter in the rim. The differences in the fitting parameters from various sources are mainly because different interatomic potentials and methods are used to obtain crater functions. Kalyanasundaram et al also used the SW potential as this work but a different method for calculation of crater function. Liedke used a Monte Carlo method to obtain the crater functions, which is completely different from the MD method as used in this work and Kalyanasundaram et al. Unfortunately, due to lack of available experimental data for crate shapes, it is impossible to tell which method gives the correct crater functions.

Additionally, the analytical form is found to be inapplicable for high angles. At high angles ($> 60^\circ$), due to highly asymmetry, the craters can not be fitted to the form of difference of Gaussians. This problem has also been reported by Liedke [19]. As a result, a modified form or even a complete new form should be employed to describe the craters.
4.3 Conclusions

The melting-quenching method, although simple, seems to be applicable to generate an amorphous silicon target with reasonable good quality. The examination of the structure of the a-Si target has revealed that the target is dense enough with the majority of the atoms having four neighbors. Although the RDF is not as exact as the real sample, it possesses the major characteristics of an amorphous sample.

The sputtering yield dependence on ion energy, ion mass and incidence angle has been investigated. In general, the MD results agree well with experimental data and TRIM simulations, which is an indication of correct setup of MD simulations.

The fitting of the crater data to the difference-of-Gaussian (DoG) form has demonstrated to be a applicable way to represent the craters. However, due to high asymmetry and irregularity at high angles, the DoG needs to be modified or a completed new form should be adopted.
In this chapter, we present a systematic study of the morphology evolution of silicon surfaces bombarded by Ar\(^+\) ions using our MD/kMC hybrid model. In order to investigate the physics of pattern formation, simulations were performed for various ion energies and incidence angles, ranging from 100 to 1000eV and 0° to 85°, respectively. The simulation results are compared with carefully selected experimental observations and the continuum theory recently developed by Norris et al [43].

First, a summary of experimental studies reported literature is presented. A screening of experimental studies for comparison with simulation results is conducted since it has been found that the ion-induced pattern formation is very sensitive to impurities.

### 5.1 Screening of experimental studies

There have been a vast number of experimental studies on morphology evolution of silicon surface due to low-energy Ar\(^+\) bombardment [28, 45, 53, 59, 129–132], as summarized in Table 5.1. The table lists the ion and the substrate parameters, and the resulting surface morphology under such experimental conditions for a better comparison between them. By careful examination, it would be found that these experimental observations are not consistent. For instance, ordered dots were observed in [131] for normal incidence, but Madi et al [28] and Castro et al [59] found the surface remained flat from normal incidence up to about 45°, which is also different from Ziberi et al [132] that found ripple formation for angles from 5° to 30°.
Table 5.1: A partial summary of experimental data for Si surface evolution under low-energy (< 2 keV) Ar\textsuperscript{+} ions bombardment

<table>
<thead>
<tr>
<th>Ref</th>
<th>$E$(eV)</th>
<th>$\theta$</th>
<th>$f$ ($10^{15}$ cm\textsuperscript{-2} s\textsuperscript{-1})</th>
<th>$\phi$(cm\textsuperscript{-2})</th>
<th>$T$(K)</th>
<th>orientation</th>
<th>Pattern</th>
<th>$l$ (nm)</th>
<th>$A$(nm)</th>
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<td>[129]</td>
<td>750</td>
<td>67.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(001)</td>
<td></td>
<td>570</td>
</tr>
<tr>
<td>[131]</td>
<td>1200</td>
<td>0</td>
<td>1.5</td>
<td>$8.63 \times 10^{19}$</td>
<td>(100)</td>
<td>Dots</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[132]</td>
<td>500-2000</td>
<td>5 - 85</td>
<td>1.87</td>
<td>$1.12 \times 10^{17}$</td>
<td>water cooled</td>
<td>(100)</td>
<td>R</td>
<td></td>
<td>, flat, pillar</td>
</tr>
<tr>
<td>[45]</td>
<td>250-1200</td>
<td>60</td>
<td>3.37</td>
<td>up to $1.6 \times 10^{20}$</td>
<td>500-750</td>
<td>(111)</td>
<td>R</td>
<td></td>
<td>to R\perp</td>
</tr>
<tr>
<td>[130]</td>
<td>500</td>
<td>60</td>
<td>4.68</td>
<td>$4.8 \times 10^{19}$</td>
<td>600-750</td>
<td>(111)</td>
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<td></td>
<td>to R\perp</td>
</tr>
<tr>
<td>[28,53]</td>
<td>250-1000</td>
<td>0 - 85</td>
<td>3.36</td>
<td>up to $8 \times 10^{18}$</td>
<td>ambient</td>
<td>(110)</td>
<td>flat, R</td>
<td></td>
<td>, R\perp</td>
</tr>
<tr>
<td>[59]</td>
<td>300-1000</td>
<td>0 - 80</td>
<td>1.82</td>
<td>$6 \times 10^{17}$</td>
<td>(100)</td>
<td>flat, R</td>
<td></td>
<td>, R\perp</td>
<td>20-60</td>
</tr>
</tbody>
</table>

Notes:
(a) $E$: energy; $\theta$: incidence angle; $f$: flux; $\phi$: fluence; $T$: temperature; $l$: ripple wavelength; $A$: ripple amplitude
(b) “R||” represents the parallel-mode ripples whose wave vector is parallel to the beam direction. “R\perp” represents the perpendicular mode ripples with wave vector perpendicular to the beam direction.
This inconsistence could be due to impurities that are supplied by either the ion source or the sample clips during irradiation. Ozaydin et al [25–27] performed real-time x-ray studies on the effect of Mo impurities on pattern formation under normal incidence. It was revealed that silicon surfaces remained smooth if the Mo impurities supplied by the sample clips were eliminated. The nanodots formation under normal incidence was due to impurities. Madi et al [28] also observed the significant effect of Mo clips on surface morphology at 30° off-normal incidence. The ripple structures only formed at the edge of the clips and became vanished in the regions that are 1 mm away from the clips. All these observations have concluded that surface pattern formation is very sensitive to impurities.

The existence of impurities would complicate the understanding of the physical origin of pattern formation. In light of this, only experiments designed carefully to eliminate possible sources of contaminants are reliable since our simulations are for pure silicon bombarded by Ar⁺. Based on this criteria, experimental observations by [28] and [59] are selected for comparison to our simulation results since the absence of impurities was confirmed in their experiments by using techniques such as X-ray photoelectron spectrometry (XPS). Also the experimental results reported by these two papers are consistent with each other, which further confirms their reliability.

5.2 Simulation parameters

The simulation surface was chosen to be a squared lattice consisted of \( L \times L \) atoms, where \( L = 200 \) or 400 for most cases, with slab periodical boundary conditions. This size of surface can well contain a few ripples since most of ripples are about 20-40 nm for ion energies below 1 keV as observed in experiments [28, 59]. The simulated ion flux was set to be \( 1.5 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1} \) that is typical in experiments. For most simulations, the fluence was \( 2 \times 10^{17} \text{ cm}^{-2} \) that is high enough to study the dynamics of pattern formation. The azimuthal angle for the ions is 22.5° to avoid artifacts.
As mentioned in Chapter 3, the MD/kMC program takes two major inputs. One is the crater function data in a format of matrix. The crater functions are obtained for incidence angles from 0° to 85° in increment of 5° ending up with 18 sets of crater functions for each ion energy. When an ion finds its impact point, the local incidence angle is calculated based on the local slope and the beam direction. The local incidence angle has to be rounded to a nearest value where the crater function is available. For instance, if the local incidence angle is calculated to be 63°, then the crater function of 65° is chosen to be landed since 65° is the nearest available crater function. The surface height nearby the impact point is then changed corresponding to the chosen crater function.

The other input is the energy barrier and the temperature for the Arrhenius diffusion equation to calculate the diffusion rates. The substrate energy barrier $E_s$ and the net bond-breaking energy $E_{nn}$ were set to be 1.65 eV and 0.62 eV, respectively, according to [100]. The temperature was initially set to be close to room temperature. However, it was found the diffusion rates were too low to cause any relaxation of the surface. This seems to be a common issue for all Arrhenius-based atomistic diffusion models. Yewande et al had to use an effective temperature as high as 1500 K for the kMC model [57, 90]. Liedke [19] used an arbitrary temperature $T = 5350$ K. They reasoned that the effective temperature was to account for the thermal spikes [92]. The surface temperature was estimated by solving the dynamic-heat-conduction temperature. It was found that the surface temperature can rise up to higher than 1200 K on average for a period time (microsecond) after an ion bombardment. This rising temperature can greatly enhanced the surface diffusion. As a result, they proposed to used an effective temperature rather than the room temperature. However, the exact effective temperature is hard to estimate since it depends on many ion and target parameters. In this work, the effective temperature was set to be 700 to 800 K.

In order to investigate the angular dependency of surface patterning, simulations of 0° to 80° incidence in 5° increments were performed for each ion energy to construct a phase diagram. The wavelength and roughness were measured as a function of
fluence to study the temporal evolution of surfaces. Furthermore, preliminary studies of pattern formation on rotated samples were performed.

5.3 Results and discussions

5.3.1 Phase diagram

A phase diagram is commonly used to describe distinct phases occurred at different conditions in material science. In this work, a phase diagram is defined as a chart showing distinct types of pattern at different incidence angles. Figure 5.1 shows the phase diagram for ion energies at 100, 250, 500, 700 and 1000 eV. Examples of different pattern types are given in Figure 5.2. For all energies, the patterns are distinguished as the following types:

- flat surface for 0° to about 35°
- transient ripples for 40°.
- well-aligned parallel-mode ripples for 45° to 70°
- short-length stripes for 75° to 80°

There are two transitions for the patterns. The first one is at about 40° where the pattern changes from flat to parallel ripples. The other one is at the glancing angle (about 75°) where the well aligned ripples are replaced by irregular short-length stripes.

The phase diagram predicted by the MD/kMC simulations corroborate well the experimental findings [28, 59] that observed the flat-to-ripple transition at about 47°. However, the simulations did not predict the formation of perpendicular-mode ripples at glancing angles (> 80°). We conjecture that this is due to the low quality of 80° crater function and the lack of crater functions for angles > 80°. The crater functions are hard to obtain due to the difficulty to determine the impact points and the extremely high ion reflection rate (100% for > 80°), leading to low ratio of signal to
Figure 5.1.: Phase diagram of various energies 100, 200, 500, 500 and 1000 eV. ×: flat; Δ: transient ripples; +: parallel-mode ripples; and circle: short-length stripes. Fluence is $2 \times 10^{17}$ cm$^{-2}$. The dashed lines mark the transition angles.
Figure 5.2.: Surface morphology of silicon bombarded by 500 eV Ar$^+$ at various incidence angles. The beam direction is indicated by the arrow. All axis units are in atomic diameter that is about 2.71 Å.
noise. Even though the perpendicular-mode was not predicted by the simulation, the formation of the irregular short-length stripes is a sign of transition.

One of the objectives of this work is to validate the theory developed by Norris et al. [43, 54] recently that associates the surface evolution with the moment of the craters. The derivation of the theory has been briefly introduced in Chapter 1. Here we just rewrite the analytical form derived by this theory:

$$\frac{\partial h(x, y, t)}{\partial t} = (S_X(\theta) \frac{\partial^2 h}{\partial x^2} + S_Y(\theta) \frac{\partial^2 h}{\partial y^2}) - B \nabla^4 h$$  \hspace{1cm} (5.1)

with the curvature coefficients are calculated by

$$S_X(\theta) = I_0 \frac{d}{d\theta} [M^{(1)}(\theta) \cos(\theta)] \hspace{1cm} (5.2a)$$
$$S_Y(\theta) = I_0 M^{(1)}(\theta) \cos(\theta) \cot(\theta) \hspace{1cm} (5.2b)$$

Where $I_0$ is the beam flux. The $B$ parameter is the coefficient for the viscous flow. The viscous flow always relaxes the surface, thus the instability of the surface is determined by the curvature coefficients $S_x$ and $S_y$. According to Equation (5.2), the first moment of the crater functions is the key for $S_x$ and $S_y$ calculation. In a discrete system, the moments of the crater functions are calculated according to

$$M_x^{(0)} = \sum_{1}^{M} \sum_{1}^{N} \Delta h(x, y) \Delta x \Delta y = \Omega Y \hspace{1cm} (5.3)$$
$$M_x^{(1)} = \sum_{1}^{M} \sum_{1}^{N} x \Delta h(x, y) \Delta x \Delta y \hspace{1cm} (5.4)$$
$$M_y^{(1)} = \sum_{1}^{M} \sum_{1}^{N} y \Delta h(x, y) \Delta x \Delta y \hspace{1cm} (5.5)$$

where $\Delta h(x, y)$ is the crater function; $\Delta x$ and $\Delta y$ are the size of small columns used in calculation of crater functions; $M$ and $N$ are the number of columns on the $x$ side and $y$ side respectively; $M_x^{(0)}$ is the zero moment that is associated with the sputtering yield $Y$ and the atomic volume $\Omega$. $M_x^{(1)}$ and $M_y^{(1)}$ are the $x$ and $y$ components of the first moment that describes the magnitude and direction of the net mass movement. Figure 5.3 displays the $M_x^{(1)}$ calculated for the crater functions
Figure 5.3.: Calculated $x$-component of the first moment of the craters obtained for various energy and incidence angles. The spline lines between data points are intended to guide the eye.

obtained in this work. The $y$-component moments are not shown here because they are close zero due to symmetry.

As shown in Figure 5.3, the moment is nearly zero at $0^\circ$ due to symmetry. The moment becomes positive at off-normal angles due to the asymmetry of the craters. The moment is the summation of positive contribution from the rim and the negative contribution from the hole. As long as the contribution from the rim is greater than from the hole, the moment is positive. The moment increases with increasing incidence angle until a maxima is reached at about $40^\circ$. Passing $40^\circ$, the moment decreases with the angle due to the elongation of the craters. At $80^\circ$, the contribution of the hole exceeds the rim, leading to a negative moment. Approximately, the moment depends linear with the ion energy for the same angle since high energies would induce larger craters.
As discussed above, the signs of the curvature coefficients $S_x$ and $S_y$ determine the ripple formation and orientation. If $S_x > 0$ and $S_y > 0$, the surface remains flat. If $S_x < 0$ and $S_y > 0$, parallel-mode ripples will form assuming the beam is parallel to x-axis. If $S_x > 0$ and $S_y < 0$, perpendicular-mode ripples will form. If both $S_x$ and $S_y$ are negative, ripples will form with orientation determined by $\max(|S_x|, |S_y|)$.

Since $\cos \theta$ and $\cot \theta$ are always positive for $0^\circ$ to $90^\circ$, the signs of $S_x$ and $S_y$ are determined by the signs of $\frac{d}{d\theta}[M_x^{(1)}(\theta)\cos(\theta)]$ and $M_x^{(1)}(\theta)$ determines.

According to Figure 5.3, it can be found that $M_x^{(1)}(\theta)$ changes its sign from positive to negative at about $77^\circ$, which means $S_y > 0$ for $\theta < 77^\circ$ and $S_y < 0$ for $\theta > 77^\circ$. In order to know the sign of $S_x$, $M_x^{(1)}(\theta)\cos(\theta)$ has to be calculated. Figure 5.4 gives the results of $M_x^{(1)}(\theta)\cos(\theta)$ showing maximum values at about $35^\circ$, which means the sign of $\frac{d}{d\theta}[M_x^{(1)}(\theta)\cos(\theta)]$ changes from positive to negative at this angle.

Since both $S_x$ and $S_y$ are negative for $80^\circ$, it is necessary to estimate their values in order to determine the ripple origination. Take the 500 eV case for example. It was calculated that $S_x = -11.85I_0$ and $S_y = -5.65I_0$. Although $|S_x| > |S_y|$, they are comparable. As a result, the resulting structures could be a mixing of both modes of ripples. The phase diagram predicted by the moment description of analytical equations is summarized in Table 5.2. The moment criterion predicts a flat-to-ripple transition at about $35^\circ$, which is in good accordance with the simulation results. Thus, our results also confirm that it is the moment of the craters that determines the pattern type and the transition angles.

<table>
<thead>
<tr>
<th>$0-35^\circ$</th>
<th>$35-77^\circ$</th>
<th>$77-80^\circ$</th>
<th>Predicted Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_x$</td>
<td>$&gt; 0$</td>
<td>$&lt; 0$</td>
<td>$&lt; 0$</td>
</tr>
<tr>
<td>$S_y$</td>
<td>$&gt; 0$</td>
<td>$&gt; 0$</td>
<td>$&lt; 0$</td>
</tr>
</tbody>
</table>

Table 5.2: Phase diagram predicted by the moment of the crater function
Figure 5.4.: $M_x^{(1)} \cos(\theta)$ of the craters obtained for various energy and incidence angles. The spline lines between data points are intended to guide the eye.
5.3.2 Role of erosion effects

The erosion effects have been considered as the major mechanism for ion-induced pattern formation for over two decades. Carter and Vishnyakov [44] were the first to challenge this erosion-based paradigm by proposing the effects of mass redistribution to account for smoothening effect at near-normal incidence. However, the effects of mass redistribution has not got enough attention until the recent development of crater function theory. The primary reason for the delay may be due to the possibility of measuring or quantifying these effects in experiments. The measurement of sputtering yield had been well established even earlier than the first discovery of sputter ripple by Navez in 1962 [10]. But the effects of mass redistribution are in sub-angstrom dimension and hard to be measured by available techniques. As a result, the mass redistribution effects were only used for qualitative explanation for the presence of flat surfaces under low off-normal incidence, as the works by Davidovitch et al [128] and Madi et al [47]. The development of crater function theory has made the quantitative analysis to be possible. The predication of exact pattern types and pattern transitions becomes practicable. The use of MD simulations provides a way to actually visualize the mass redistribution effects that is shown like a crater at nanoscale. The crater data can then be combined with either continuum theory [43, 52, 54], or numerical integration [96] or atomistic KMC model [98] to study the surface morphology evolution. These works have demonstrated that erosion is essentially negligible or even irrelevant at least for low and intermediate angles. The erosion-based paradigm has been urged to be replaced with a redistribution-based paradigm [43]. However, it is still not clear whether erosion is relevant for perpendicular ripple formation at glancing angles. In order to elucidate the role erosion effects at high angle, we conducted simulations using erosive-only crater functions for the case of 500 eV Ar⁺.

The crater functions obtained in Chapter 4 are the summation of the erosive and the mass redistributive contributions. In order to separate these two effects,
the erosive crater functions were also obtained by a way similar to the one for the composite crater functions. For every impact, the height of the location where the sputtered atom is originated is reduced by 1. By averaging over 1000 impacts, the erosive crater functions are obtained. A few examples are shown in Figure 5.5 for 20°, 40°, 60° and 80°. As expected, an erosive crater only contains a hole whose depth increases as increasing angles until 65°, which shares the same trend of sputtering yield with respect to incidence angles. The hole also becomes elongated as increasing angles.

With the other simulation parameters remaining the same, the surface evolution was simulated using the erosive crater function. The resulting topographies are can be distinguished as the following types, as shown in Figure 5.6:

- At 0°, the surface is almost flat;
- From 5 to 30°, the surface appears as randomly arranged holes that ensemble the experimental findings as shown in Figure 1.3(b), which may suggest the possibility of formation of random holes under erosion-driven systems;
- From 35 to 50°, irregular short-length perpendicular-mode ripples;
- From 55 to 85°, well-aligned perpendicular-mode ripples.

It is distinct that the patterns are completely different from the ones simulated using composite craters. Particularly, the formation of well-aligned perpendicular-mode ripples at glancing angles is a sign that erosion is the dominant role in pattern formation at high angles.

In order to understand the origin of these patterns, the moment of the erosive contribution together with the redistributive contribution and their total were calculated, as shown in Figure 5.7. The magnitude of the erosive moment is at least an order of magnitude smaller than the redistributive moment, but their magnitudes are comparable at high angles (> 70°). To better associate the moment with pattern type, the curvature coefficients \( S_x \) and \( S_y \) contributed from erosive part are displayed
Figure 5.5.: Examples of erosive crater functions. The beam direction is from left to right and the impact points are at (0,0). All axis units are in atomic diameter.
Figure 5.6.: Phase diagram of simulation results using erosive crater functions. The beam direction is indicated by the arrow. All axis units are in atomic diameter.
Figure 5.7.: The moment of the erosive part, the redistributive part and their total. The spline lines are to guide the eye.

in Figure 5.8. $S_y$ is negative for all angles, which implies the surface is destabilized at all angles. $S_x$ has a turn point at 65° where its sign is changed. $S_x$ and $S_y$ are comparable for angles $< 15^\circ$. This may lead to holes formation. $|S_x| > |S_y|$ for 20-60°, which means parallel-mode ripples should form. This is not in agreement with the simulation results. $S_x$ becomes positive for angles $> 65^\circ$, indicating the formation of perpendicular mode ripples, which agrees well with simulation results.

Although the agreement between moment analysis and simulations is not exact, three conclusions can be drawn from the simulations of erosive craters. Firstly, erosion is irrelevant for the flatness of surfaces at $\theta < 40^\circ$, since its contribution to the curvature coefficient $S_x$ is in the wrong sign. Secondly, it is negligible for the parallel ripple formation for $40^\circ < \theta < 65^\circ$ because its contribution to $S_x$ is an order of magnitude smaller than redistributive contribution. Thirdly, erosion is the physical origin for perpendicular mode ripple formation at high angles.
Figure 5.8.: the curvature coefficients $S_x$ and $S_y$ contributed from erosive part. $I_0$ is the beam flux. The spline lines are to guide the eye.

5.3.3 Temporal evolution: ripple coarsening and propogation

No studies have yet been reported to investigate the temporal evolution using the redistribution-based paradigm. However, the current moment-description analytical equation [43] is only valid for linear regime due to the two main approximations made in its derivation. One is the truncation of high-order moments terms in the serial expansion of prompt redistributive integral, leaving only the first-order term. The other one is the small angle approximation that assumes the surface is nearly flat. These two approximations limit the reliability of the current linear theory to account for surface evolution in nonlinear regime. As the structures evolve larger and taller as bombardment goes, these two approximations begin to break down. Our MD/kMC model is developed in a way that is free of such approximations. As a result, it can nicely compensate the drawbacks of the analytical theory to study both linear and nonlinear regimes.
The simulation was performed for 500 eV Ar\(^+\) at 60\(^\circ\) incidence angle. The flux was chosen to be \(2 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}\) to ensure to cover the linear regime. The fluence was up to \(5 \times 10^{17} \text{ cm}^{-2}\). Snapshots of the surface profile were output every \(2 \times 10^{14} \text{ cm}^{-2}\) for fluence \(< 3 \times 10^{16} \text{ cm}^{-2}\) and every \(5 \times 10^{15} \text{ cm}^{-2}\) for the rest of simulation time. The surface roughness, amplitude and wavelength of ripples were calculated for every snapshot.

Profiles of the surface topography at various fluence are shown in Figure 5.9. At low fluence (\(\sim 10^{14} \text{ cm}^{-2}\)), the surface is almost flat. But with careful examination, it can be found that very small ripple-like structures are formed locally, serving as “ripple seeds”. With increasing fluence (\(\sim 2 \times 10^{15} \text{ cm}^{-2}\)), clear ripples that develop from the ripple seeds become to appear. As bombardment continues, the amplitude of the ripples starts to grow larger and larger but with the wavelength nearly constant. At around \(10^{16} \text{ cm}^{-2}\), the wavelength of the ripples also start to grow, indicating the start of coarsening. The amplitude and wavelength of the ripples reaches saturation at around \(10^{17} \text{ cm}^{-2}\). After this point, the ripples become more and more aligned and the defect density of the ripples become lower and lower.

The temporal evolution of the amplitude and wavelength are displayed in Figure 5.10. Basically, the evolution can be divided into three regimes as marked in Figure 5.10(b). In the linear regime (\(< 10^{16} \text{ cm}^{-2}\)), the wavelength is constant and the amplitude grows exponentially (Figure 5.11), which behaves like BH ripples. This is reasonable because the moment-based continuum equation shares the same form with BH linear equation. For fluence larger than \(10^{16} \text{ cm}^{-2}\), the surface evolution enters the nonlinear regime. Between \(10^{16} \text{ cm}^{-2}\) and \(10^{17} \text{ cm}^{-2}\), the surface undergoes coarsening. We conjecture that the ripple coarsening is caused by the different propagation speed of ripples. Ripples are traveling with a speed \(v = -\frac{\partial M^{(0)}}{\partial \theta} \propto \frac{\partial \gamma}{\partial \theta}\), where \(M^{(0)}\) is the zeroth moment. The speed of each ripple is different due the diversity of ripples in shape. As a result, the ripples traveling faster will catch up with the slower ones and merge together to form larger ripples. Starting from \(10^{17} \text{ cm}^{-2}\), the amplitude and wavelength reach saturation that is considered due to the asymmetric crater rims
Figure 5.9.: Temporal evolution of surface profile at different fluence. The unit of the fluence is cm$^{-2}$. 
creating downhill mass movement that increases with increasing incidence angles [96]. Note that the wavelength obtained by our simulation is about 3 to 4 times smaller than experimental finding. This is mainly due to the drawback of the kMC model that will be discussed in details in Section 5.3.5

Another way to study the nonlinear surface evolution is the use of dynamic scaling theory [16]. The dynamics of a surface can be quantified by the root-mean-square fluctuation of the surface height $h(x, y, t)$, namely the interface width, defined as

$$W(L, t) \equiv \sqrt{\frac{1}{L^2} \sum_{x,y=1,L} [h(x, y, t) - \bar{h}(t)]^2}$$ (5.6)

where $L$ is the system size and $\bar{h}(t)$ is the mean surface height, defined by

$$\bar{h}(t) \equiv \frac{1}{L^2} \sum_{x,y=1,L} h(x, y, t)$$ (5.7)

According to Family and Vicsek [133], the interface width $W(L, t)$ follows

$$W(L, t) \sim L^\alpha f \left( \frac{t}{L^z} \right)$$ (5.8)

The growth of $W(L, t)$ is distinguished at different time regimes, given by

$$W(L, t) = \begin{cases} 
    t^{-\beta} & \text{if } t_0 \ll t \ll t_s \\
    L^\alpha & \text{if } t \gg t_s
\end{cases}$$ (5.9)

Where $t_0$ is the initial state, and $t_s$ is the saturation time. The scaling parameters, $\alpha$, $\beta$, and $z$, are the roughness, growth, and dynamic exponents, respectively. Thus, according to the scaling theory, the interface width is in power law dependence of roughness with time in the early times and becomes constant in the late times.

The scaling theory can be used to define “universality classes”. As pointed out in [16], “different physical problems can be divided into different universality classes according to the form of the nonlinear differential equation that governs the interface evolution. Each universality class has its own set of scaling exponents. Therefore, by measuring the scaling exponents experimentally and comparing them with theoretical predictions, one can identify the universality class that the system belongs to and
Figure 5.10.: Temporal evolution of (a) amplitude and (b) wavelength. The dashed line marks the saturation point.
Figure 5.11.: Sketch showing the exponential growth of amplitude at linear regime. Note the $y$-axis is with $\log_e$ scale.
Figure 5.12.: Sketch showing the interface width as a function of ion fluence for 500 eV Ar\(^+\) bombardment of Si. The dashed line indicates the saturation fluence or time.

predict the dominant mechanism for surface evolution”. In other words, the scaling theory bridges the experimental measurements and the identification of dominant mechanism with the scaling exponents.

The interface width of this simulation was measured and plotted in Figure 5.12. The surface grows exactly as predicted by the scaling theory. The growth exponent \(\beta\) is yielded to be 0.358, which is very close to the experimentally measured value 0.32 in \([59]\) for 700 eV Ar\(^+\) at 55°. This is probably an indication that our MD/kMC has already included the correct physical mechanism for surface diffusion.

5.3.4 Ripple wavelength dependence on incidence angle and ion energy

The angular dependence of ripple wavelength at fixed energy (500 eV) is presented in Figure 5.13. The general trend is that the wavelength decreases with increasing angle. Similar trend was reported in experiments for 700 eV \([59]\).
Figure 5.13.: Ripple wavelength dependence on incidence angle for 500 eV Ar\(^+\) on Si. The line is to guide the eye.
Figure 5.14 shows the wavelength dependence of ion energy for fixed incidence angle ($60^\circ$) for low fluence ($10^{16}$ cm$^{-2}$) that is within the linear regime. In general, the wavelength is larger for higher ion energy and seems to be linear with the ion energy, i.e., $\lambda \sim E$, which is also observed in experiments [59]. According to the linear moment-based continuum theory (Eq 5.1), the characteristic wavelength is given by

$$\lambda^* = 2\pi \sqrt{\frac{2B}{-S}}$$  \hspace{1cm} (5.10)$$

where $S$ and $B$ are coefficients for the curvature term and viscous flow term, respectively. For our model, the $B$ is the coefficient of the ion-enhanced diffusion. The density of the defects on the surface is about proportional to the ion energy, which makes the effective diffusivity to be proportional to the ion energy. As a result, it is reasonable to assume that $B \propto E$. From Figure 5.4, it can be obtained that $|S| \propto E^{-1}$. Thus, the dependence of the wavelength would be

$$\lambda^* \propto \sqrt{\frac{E}{E^{-1}}} = E$$  \hspace{1cm} (5.11)$$

5.3.5 Shortcomings of current diffusion model and effects of relaxation mechanisms

Although the simulation results corroborate well the experimental findings and the predictions by the moment-description continuum theory for many features of the surface evolution, the ripple wavelength and amplitude are predicted incorrectly. The wavelength predicted by the simulations is about 3-4 times smaller than the experimental observations. On the other hand, the amplitude is overestimated by about 50% on average. Such mismatch poses concerns towards to the validity of the kMC diffusion model. Thus, it is necessary to inspect the possible reasons for such mismatch and their effects on surface evolution.

The issue of incorrect wavelength and amplitude is common for the models that employ kMC diffusion approach, such as in [56, 57, 90, 94]. The short wavelength and high amplitude are indications of weak smoothing force. In other words, the $B$
Figure 5.14.: wavelength dependence of ion energy for fixed incidence angle (60°) for low fluence ($10^{16}$ cm$^{-2}$).
term in the continuum theory is underestimated compared to real value. However, the underestimation of $B$ term would not impair the studies of pattern formation, because it is the curvature dependence of mass redistribution, rather than diffusion or viscous flow, that determines the pattern types, as demonstrated in the moment-description continuum theory [43]. The smoothing process only mediates the surface roughness to achieve right wavelength and amplitude. In one of our simulations, the diffusion was turned off by setting $T = 0$ K. The simulation yielded the same phase diagram as the one with diffusion, except unrealistic ripple amplitude. Thus, as long as the simulations are to study different effects on pattern formation, the underestimation of $B$ term does not make the simulations invalid. However, it limits the exact output of wavelength, amplitude and saturation fluence from the simulations.

The underestimation of smoothing force can be caused by several reasons. One is the relatively high value of the binding energy $E_{nn}$ used in the calculation of the activation energy. The binding energy determines the probability of atoms to reduce its coordination number. With the binding energy used in this work, almost all (>$99.99\%$) of the diffusions are the point defect diffusion or diffusion along the edge diffusion. Consequently, once an atom binds to another atom or a cluster, it is almost impossible for the bond to break. This effect dramatically reduce the downhill current that relaxes the surface. Using lower binding energy is an option to tackle this issue, but it renders the simulation unphysical. The second reason is that surface diffusion may not be the dominant driving for relaxation. It is known that an amorphous layer is formed when a semiconductor is under ion irradiation. The ion-irradiation-enhanced viscous flow has been considered to be the dominant smoothing mechanism over thermally-activated surface diffusion for energy regimes ranging from keV to MeV near room temperature [50, 71]. However, the viscous flow is difficult to model atomistically. The viscous flow is driven by the surface stress. As a result, the interactions between atoms must be modeled for the whole system in order to produce correct stress, which is too computationally demanding. Thus, numerical way seems to be the only choice to correctly model this process.
5.3.6 Pattern formation on rotated samples

Irradiating a substrate with simultaneous substrate rotation can generate patterns, including quantum dots and curved ripples [15]. Thus, it would be interesting to inspect what patterns can be produced by the kMC/MC model with sample rotation. The sample rotation was modeled by changing the azimuthal angle with a speed associated with the rotation speed. The simulations were performed for 500eV Ar\(^+\) at various incidence angles and different rotation speed. Figure 5.15 gives the comparison of patterns with and without rotation at 10\(^\circ\), 40\(^\circ\) and 65\(^\circ\) with a fixed rotation speed of 1.257 rad/s. Arrays of squared dots are formed for 40\(^\circ\) and 65\(^\circ\) with rotation. The patterns generated with sample rotation are strongly related to patterns without rotation. If ripples are not formed without rotation, then the surface remains flat with rotation as the 10\(^\circ\) case. The size and the spacing of the squared dots also depends on the wavelength of the ripples formed without rotation in a linear scale.

Squared dots are not always formed. Figure 5.16 shows the surface profiles at different fluence at 65\(^\circ\) incidence with a rotation speed of 0.126 rad/s that is 10 times slower than previous value. Unwell ordered ripples, instead of dots, are formed. Interestingly, the ripple orientation also rotates as the sample rotates. It can be interpreted that when the rotation speed is very slow, the incident angle can be seen as almost constant for a period of time. During this period, the ripple can form. Thus, the rotation speed affects the pattern in a on/off way. There is a dividing value for the rotation speed. When the rotation speed is larger that this critical value, square dots are formed. Increasing the speed cannot improve the ordering of the dots. When the speed is smaller than this value, rotated ripples are formed. This critical rotation speed is found to be around 0.5 rad/s.
Figure 5.15.: Comparison of patterns with and without rotation at 10°, 40° and 65° with a fixed rotation speed of 1.257 rad/s. The size of each image is 250 lattice cells.
Figure 5.16.: Surface profile at different fluence at 65° incidence with a rotation speed of 0.126 rad/s. The size of each image is 250 lattice cells.
6. SUMMARY AND FUTURE DIRECTION

6.1 Summary and conclusions

The formation of self-organized structures by ion beam sputtering (IBS) is an intriguing phenomenon, mainly for its potential application in nanofabrication. A wide range of structures can be induced just by tuning ion irradiation parameters and target parameters. To better control this technique, the underlying mechanisms must be understood. However, despite lots of experimental and theoretical efforts in the past few decades, there are still many basic questions open to discussion. The difficulty is mainly due to the huge time- and spatial separation of the concurrent physical processes involved in pattern formation. For each individual ion, the interaction with the target atoms is only within a period of tens of ps and within a spatial region of a few nm. In contrast, the gradual relaxation processes can takes up to seconds and minutes. And the resulting surface features are also a few order of magnitude larger than the size of the collision cascade.

For the past two decades, the understanding of the ion-induced pattern formation is primarily relied on the erosion-based paradigm that was proposed by Bradley and Harper in 1988 [11]. Erosion is considered to always destabilize a surface by eroding valleys faster than hills due to more energy deposited at the hills. Although the BH theory succeeds in explaining some features of the ripple formation, it fails to explain the occurrence of ion-induced smoothening at near off-normal incidence ($< 45^\circ$ for Ar$^+$ on Si). Recently, the development of the crater function theory has advanced the knowledge of ion-induced surface evolution by accounting for the effect of mass redistribution. The ion impacts do not only cause ejection of atoms, but also cause atom moving laterally, leading to surface height response resembling craters at sub-angstrom scale. Erosion has been proved to be irrelevant to the pattern formation...
at low and intermediate incidence angles. Instead, the mass redistribution is the dominating mechanism. The crater function theory has overturned the erosion-based paradigm to a redistribution-based paradigm.

The development of the moment-description continuum theory has further elucidate that the first moment of the crater functions contains the most important information that can determine the pattern type [43]. However, all the current versions of crater functions have yet to explain the role of erosion at glancing incidence angles. Besides, there have not been studies that use crater function theory to inspect the surface evolution in the late stages. The applicability of the current moment-based theory in the late stages is questionable due to its small-slope approximation and truncation of high order moment terms.

The hybrid MD/kMC atomistic model developed in this work is aimed to provide an alternative way to study the surface evolution. Unlike the continuum theory, the model is fully atomistic. The model is designed in a way that mimicks a real bombardment experiments. Ions are considered to generated at random location. The impact point is determined by ray tracing the ion. Once the ion is landed on the surface, the surface height nearby the impact point is changed according to the corresponding crater function. The smoothing process is modeled using a kMC Arrhenius diffusion approach that has been shown to be a good atomistic representation of surface diffusion by previous studies.

Using this model, a systematic study was performed for silicon bombarded by Ar$^+$ ions of various energies. Since the resulting patterns are sensitive to the craters, the procedure of obtaining crater functions was carefully conducted and examined. The a-Si target was prepared using melting-quenching method due to its widely use and its computational efficiency. The structures of the a-Si target was characterized and compared to experimental data. Its density of the a-Si is identical to experiments. The majority of its coordination number is 4. Its RDF is in good agreement with experimental findings in general. All of these properties show that the a-Si generated in this work is of good quality and can be used to obtain crater functions.
The analysis of the sputtering yield further confirmed the quality of the a-Si target. The accuracy of the sputtering yield relies strongly on how energies transfer on the surface. Thus, if the sputtering yield is in good agreement with experiments, it is also an indication of proper simulation of mass transportation on the surface that is directly related to the formation of crater functions. The energy, angular and mass dependence of sputtering yield were analyzed and found to in good accordance with experimental data and SRIM calculations.

Fitting the crater function to an analytical form was also attempted. The analytical form provides the possibility to share the crater data, and thus is important to investigate. The difference-of-Gaussian form seems to work fine with angles $< 50^\circ$. However, a modified or new form is needed for higher angles due to large asymmetry of crater functions at high angles.

Simulations using the MD/kMC model were performed for Ar of energy 100 eV, 250 eV, 500 eV, 700 eV and 1000 eV at incidence angles of 0° to 80° with fluence up to $10^{18}$ ions/cm$^2$ to cover both the linear and nonlinear regimes. The major findings are listed as follows:

1. The phase diagram shows that flat surfaces are formed for $\theta < 40^\circ$, which corroborate with experiments. The calculation of crater moment further confirms that erosion is irrelevant in the formation of flat surface for $\theta < 40^\circ$ and is negligible in the formation of ripples or $40^\circ < \theta < 75^\circ$. The formation of perpendicular ripples were not observed, which is contradicted to the predication of the moment-based theory. However, perpendicular ripples are found to formed in the simulations using erosive crater functions. The results elucidate that erosion plays the dominant role in ripple formation at glancing angles.

2. The temporal evolution of surface morphology reveals that the ripples undergo linear growth in the early regimes. Ripple coarsening happens when the fluence passes $10^{16}$ cm$^{-2}$ due to different traveling velocities of the ripples, leading to merging of small ripples. The wavelength and amplitude ceases to grow at
around $10^{17}$ cm$^{-2}$. The surface roughness obeys the scaling theory and yields the growth exponent $\beta = 0.358$, which is very close to the experimental finding.

3. The ripple wavelength is found to decrease with $\theta$ and increase with ion energy.

4. Ion irradiation with simultaneous sample rotation generates new type of structure, i.e., the formation of arrays of squared ordered dots. The rotation speed and the pattern types formed without sample rotation affect strongly the pattern formation with rotation. The critical rotation speed is found to be about 0.5 rad/s for the irradiation conditions used in this study.

6.2 Future directions

Efforts should be devoted to address the issue of incorrect predication of wavelength and amplitude, as discussed in Section 5.3.5. Incorporating with viscous flow is a possible solution. However, since the viscous flow is difficult to model atomistically, it has to be a numerical approach like the one used in [96].

Establishing a reliable way to obtain crater functions at glancing angles is also crucial. The crater function obtained at 85° in this work was merely noise. Currently, the reason for such high noise is unknown. Without reliable crater functions at glancing angles, it is hard to judge if the moment criterion is valid at high angles.

The current crater functions are all obtained for flat surfaces. However, when structures form, the surface can not be considered as flat. As reported by Nietiadi and Urbaskek [134] recently, the surface curvature strongly affects the crater function. Thus, it is worth to obtain crater functions for different curvatures and investigate their effect on resulting morphology.
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Fields of Research Interest

Ion beam modification of materials, Surface patterning, Computational material