CHAPTER 2

THEORETICAL REVIEWS ON IONS-MATTER INTERACTIONS AND NANOPATTERNING

2.1 INTRODUCTION

The interaction of energetic ions with the material changes the properties of a material. These changes occur due to the energy loss of the incoming ion inside the sample throughout its traversal path. The spatial distribution of the ions will depend upon the ion energy and the stopping (nuclear and electronic) processes of the ions inside the material. The nuclear collisions can cause the displacement of target atoms from their regular lattice sites. A single energetic heavy ion can lead to the displacement of several tens, or even hundreds, of lattice atoms within the volume surrounding the ion trajectory. This is termed as collision or displacement cascade. As a consequence, ion irradiation can create considerable structural damage to the material. The nuclear collision of ions can sometimes lead to the ejection of surface atoms from target through the process of sputtering. This phenomenon of sputtering can cause surface erosion and can also sometimes produce self-assembly of nano structure on surfaces.

The interaction of the ion with material plays a deciding role in the ion beam-induced material modifications. The effect of ion beam on the material depends on the energy of the ions, number of ions falling per unit area (fluence) and ion species. These interactions can be classified as inelastic interactions with target electrons and elastic interactions with screened target nuclei. The former interaction is responsible for the electronic stopping (dE/dx)_e, which
dominates at high velocities, the latter for the nuclear or atomic stopping power \( (dE/dx)_n \), which dominates at low velocities \([2.1, 2.2]\). Heavy ions such as Ag and Au with high energy (1 MeV/nucleon) are often referred as swift heavy ions (SHI), as they move with velocities comparable with the Bohr velocity of electrons. SHI are capable of producing modifications in materials due to their large electronic excitation, whereas, low energy ions develop displacement cascades inside the solids. Within these cascades, atoms are ejected from their stable site in the target with a kinetic energy from 10 eV to a few 100 eV, thus, low-energy ion beam gives rise to sputtering (i.e. ion beam sputtering or IBS) or erosion of solid surfaces.

![Figure 2.1: Nuclear (red line) & electronic energy losses (black line) of Ar ions in Si.](image)

In the fig. 2.1, the energy loss of Ar ions in Si is shown. It is clearly visible that the nuclear energy loss dominates up to energies ~ 200 keV and then it falls off and electronic energy loss dominates up to few 100s of MeV and then falls down. This peak is called Bragg peak (shown with an arrow).

**2.1.2 STOPPING OF IONS**
When an ion is travelling along a path $x$ through matter as shown in fig. 2.2, the ion will continuously lose its energy due to the interaction with electrons and screened nuclei.

![Figure 2.2: Schematic of energy loss of an ion after travelling a distance $dx$.](image)

The energy loss per unit path length is denoted as stopping power, $P$

$$P = -\frac{dE}{dx}$$  \hspace{1cm} (2.1)

Normalizing the stopping of ion to the atomic density ‘n’ of the material used, the stopping cross section, $S$ can be written as

$$S = -\frac{1}{N} \frac{dE}{dx}$$  \hspace{1cm} (2.2)

where $N$ is the number of atoms per unit volume for a traversed path length $x$.

And the total stopping is composed linearly from nuclear and electronic stopping:

$$S_{\text{tot}} = S_n + S_e$$  \hspace{1cm} (2.3)

where $S_e$ and $S_n$ are the electronic and the nuclear stopping powers or energy losses, respectively.

2.1.3 ION RANGES
The projected ion range in solid is defined as the mean depth from the target surface at which the ion comes to a halt. The range of an ion in a solid can be expressed by the rate of energy loss \( \frac{dE}{dx}_{total} \) along the trajectory of the ion.

\[
R = \int_{E}^{0} \frac{1}{\frac{dE}{dx}_{total}} dE
\]  

(2.4)

where \( R \) is the range of an ion of the energy \( E \). The main parameters governing the range are the energy \( E \) and the atomic number \( Z_1 \) of the ion and the atomic number \( Z_2 \) of the target. As a consequence of stopping and scattering, each individual incident ion forms a random trajectory as shown in fig. 2.3. The range along the path is the total distance the ion incident at an angle \( \theta \) with energy \( E \) traversed along the trajectory.

**Figure 2.3: Schematic of ion range of an incoming ion incident at angle \( \theta \) with energy \( E \).**

Stopping defines the total path length \( R_t \) covered by the ion before coming to rest, \( R \) is the longitudinal range or longitudinal straggling and \( R_\perp \) is the lateral range or lateral straggling of the ion. Generally, range ‘\( R \)’ is used since it characterizes the implantation depth with respect to the surface and \( R \) is equal to \( R_\perp \) for normal incidence. The energy loss phenomenon is statistical in nature as the collisions between projectile ions and target atoms are random. All ions penetrating the solid do not have the same penetration depth, but there is distribution
along its path called longitudinal straggling. Since each successive collision of projectile ion with target atoms leads to deviation from its straight-line path resulting in a straggling in lateral direction called lateral straggling.

2.1.4 NUCLEAR ENERGY LOSS

Nuclear energy loss ($S_n$) is the transfer of energy from ion to the target during the elastic collision of ion with lattice atoms where the conservation of energy and momentum holds true. Nuclear collisions usually involve large discrete energy transfer and significant angular deflections of the ions from their trajectory. The energy deposited through these collisions result in the production of lattice disorder by the displacement of atoms from their equilibrium positions. These displaced atoms sometime have sufficient energy to cause cascade of secondary displacements of the secondary atoms to form a tree of disorder along the ion path. When the concentration of displaced atoms per unit volume approaches the atomic density of a semiconductor, the material becomes amorphous. Ion fluence also plays a crucial role in the defect formation. At low fluences, disordered zones created by different ions remain generally well separated from each other. However, as the fluence increases, these zones start overlapping leading to the amorphisation of the material. These collisions are treated as binary collisions due to their lower frequency. Nuclear energy loss process dominates at low ion energies (~ 0.1 MeV/nucleon) (see region I of fig. 2.1).

For deriving the nuclear energy loss, there are two main assumptions which need to be taken into account:

(i) Simple Screened Coulomb Potential and

(ii) Impulse Approximation

The interaction potential between two atoms $Z_1$ and $Z_2$ can be written in the form of screened Coulomb potential in low velocity collisions, the impact parameter is sufficiently large so that
the nuclear charge is screened by the electrons and it leads to a modification of the scattering potential using the screening function,

\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \chi \left( \frac{r}{a} \right) \]  

(2.5)

where \( a \) is the Thomas-Fermi screening radius for the collision

\[ a = \frac{0.885 \alpha_0 \left( \frac{1}{Z_1^2} + \frac{1}{Z_2^2} \right)^{\frac{3}{4}}}{f} \]  

(2.6)

The values of \( a \) lie between 0.1 and 0.2 Å for most cases of interactions. In Moliere approximation, screening function can be written as

\[ \chi \left( \frac{r}{a} \right) = \frac{a}{2r} \]  

(2.7)

The impulse approximation is appropriate for the small angle large impact parameter collisions that dominate the sequence of scattering which determine the charged particle trajectory. Using the impulse approximation and screened Coulomb potential, the cross section for transfer of energy between \( T \) and \( T + dT \) is given by

\[ d\sigma = \frac{\pi Z_1 Z_2 e^2 a}{8 \sqrt{\frac{M_2}{M_1} E}} T^{-\frac{3}{2}} dT \]  

(2.8)

The projectile ion moving with energy of the order of few keV/nucleon interacts with screened or unscreeened nuclei of the target atoms. The energy loss \( dE \) of an ion by elastic nuclear interaction, in a layer of thickness \( dx \), is proportional to the atomic density \( N \) as well as the total energy transferred in all-individual collisions \( T_n \) [2.3]. Considering the interaction occurring between particles (ions) with energy \( E \) and target nuclei, the probability \( P(E) \) that a particle with energy \( E \) will transfer an amount of energy between \( T \) and \( T + dT \) to a target atom is given by [2.4]

\[ \frac{dP(E)}{dT} dT = N dx \frac{d\sigma(E)}{dT} dT \]  

(2.9)

where \( E \) is the energy of the projectile particle (ion), \( T \) is the amount of energy transferred in colliding with target nuclei.
The average energy loss by the moving particle in the distance $dx$ is obtained:

$$< dE > = \int T \frac{dP(E)}{dT} dT = N \int T \frac{d\sigma(E)}{dT} dT \quad (2.10)$$

For infinitesimal $dx$, the nuclear energy loss is:

$$\left[ \frac{dE}{dx} \right]_n = N \int_{T_{\text{min}}}^{T_{\text{max}}} T \frac{d\sigma(E)}{dT} dT \quad (2.11)$$

The power limit in the integration $T_{\text{min}}$ is the minimum energy transferred, and needed to be zero. $T_{\text{max}}$ is maximum transferable energy and is given by:

$$T_{\text{max}} = 4 \frac{M_1M_2}{(M_1 + M_2)^2} E \quad (2.12)$$

where $M_1$ and $M_2$ are the masses of the projectile ion and the target atom, respectively.

Putting the value of $d\sigma$ from equation (2.1.8) and $T_{\text{max}}$ from equation (2.12) in equation (2.11), the expression for nuclear energy loss comes out to be

$$\left[ \frac{dE}{dx} \right]_n = N \frac{\pi^2}{2} Z_1Z_2e^2a \frac{M_1}{(M_1 + M_2)} \quad (2.13)$$

In the higher energy regime, the contribution of nuclear energy loss is insignificant.

### 2.1.4.1 THE COLLISION CASCADES

Nuclear collision do not only contribute to the energy loss of fast ions and determine their angular distributions, but also transfer energy to the atoms of the material, thus creating "primary" recoil atoms. If the transferred energy is sufficiently large, these primary recoils will move along a trajectory similar to that of the incident ion, and may again undergo nuclear collisions, thus creating further generations of recoils and forms a collision cascade [2.5]. Therefore, each of the recoil atoms may come to rest after covering some distance from its original site as shown schematically in fig. 2.4.
Figure 2.4: Trajectory and associated recoil atoms of the incident ion.

Depending on the amount of deposited energy per unit volume, the collision cascade may be more or less dense. Three regimes can be defined to explain the cascade formation as shown in fig. 2.5.

In single collision regime (fig. 2.5a), which is for light ions at low energy, a cascade does not really develop and the atomic motion is stopped after a few collision events. In the linear cascade regime (fig. 2.5b), collisions take place essentially only between fast particles and atoms being at rest. As the single collision regime, it allows to treat the cascade as a sequence of two-body collisions. In contrast, in the thermal spike regime (fig. 2.5c) the cascade
becomes so dense that collisions between fast particles play significant role and all lattice atoms within the cascade become a thermal ensemble with a high temperature, which may exceed the melting temperature of the solid and even its evaporation temperature on a short time scale.

2.1.5 ELECTRONIC ENERGY LOSS

Electronic energy loss \( S_e \) is the transfer of energy due to electronic collisions which occurs when the ion interacts with electrons of lattice atoms and leads to excitation and ionization. Electronic collisions involve very small energy-losses per collisions, negligible deflection of the ions trajectory, and negligible lattice disorder. In addition to stopping, the electronic interaction of an ion passing through matter results in charge changing collisions, so that the actual charge state of a fast ion in matter fluctuates continuously and is determined by a balance between electron loss and electron attachment. The average charge of the ion, which depends on its velocity, is denoted as “effective” charge, \( Z_{\text{eff}} \), and is quickly established (typically within some nm) when an ion of any charge state impinges onto a solid surface.

In the limit of very low energy, the ion becomes neutral with a vanishing effective charge (region II in fig 2.1). At high velocities (region III in fig 2.1), the projectile starts getting stripped-off its electrons and loses all its electrons when \( v \geq v_o Z_0^{2/3} \) and the ion, could be visualized as positive point charge \( Z_{\text{eff}} = Z_0 \) moving with velocities greater than the mean orbital velocity of atomic electrons in the target. Due to high ion velocity, the influence of the incident particle causes small perturbation to the electron cloud. This picture leads to the Bohr’s theory of stopping power. Bohr and others assumed that ion lose only those electrons whose orbital velocity will be less than the velocity of projectile ion. The effective charge of an ion as estimated by Bohr is given by [2.6],

\[
Z_{\text{eff}} = Z_0 \left[ 1 - \exp \left( -\frac{v}{v_o} Z_0^{2/3} \right) \right] \tag{2.14}
\]
with upper limit of velocity defined as \( Z_{oo}^{eff} = Z_0 \).

At ion velocities, \( v < v_o Z_{oo}^{2/3} \), as per the calculation given by Lindhard and Scharff [2.4], the electronic stopping power is given by:

\[
S_e(E) = 3.83 \frac{Z_{oo}^{7/6} Z_2}{(Z_0^{2/3} + Z_1^{2/3})^{3/2}} \left( \frac{E}{M_0} \right)^{1/2} = K_e E^{1/2} \quad (2.15)
\]

Or,

\[
S_e(E) \propto v_{ion}
\]

The stopping power is proportional to ion velocity.

At higher ion velocities, \( v \geq v_o Z_{oo}^{2/3} \), Bethe and Bloch [2.7] obtained the electronic energy loss as

\[
S_e = \frac{2Z_0^2 e^4}{E} N Z_1 \left( \frac{M_0}{m_e} \right) \ln \frac{2m_e v_{ion}^2}{I} \quad (2.16)
\]

Thus, after Bragg peak (fig. 2.1) the electronic stopping cross-section decreases with increasing the velocity of projectile ions as a first approximation of Bethe-Bloch formulation.

In general, electronic stopping power can be divided into two regions: the low velocity, where the projectile is only to some extent ionized and the stopping is proportional to \( v_{ion} \), the other is where the velocity is high and the projectile is fully stripped, leading to the inverse square relation of velocity with stopping power.

### 2.1.6 SPUTTERING

When a collision cascade intersects the surface, sufficient energy can be transferred to a surface atom to overcome its binding to the surface, so that it will be ejected from the solid [2.8, 2.9]. The sputtering process depends on several parameters such as the nature of the target, type of ion, ion energy, incidence angle, ion flux (rate of incoming ions towards the target per unit area) and total fluence (or dose).

**Sputtering yield**

Sputtering process is quantified by the sputtering yield (\( Y \)). It is defined as the average
number of target atoms ejected per incident ion [2.10].

\[ Y = \frac{\text{atoms removed}}{\text{number of incident particle}} \]  \hspace{1cm} (2.17)

Y strongly depends upon the transfer of energy to the atoms by incident ion. It is function of energy of ion, angle of incidence, mass of ion and target atom and target material properties as the surface binding energy of atoms in the target etc. Sputtering yield rapidly increases with increasing ion energy until reaching a broad maximum (in the 10-100 keV range) and, then, gradually decreases for very high energies (in the MeV range) [2.11]. Depending on projectile energy loss, different scenario of sputtering occur, that include material removal due to atomic collision cascade due to nuclear energy loss, so called nuclear sputtering and electronic sputtering governed by electronic excitation and ionization at higher energies due to electronic energy loss process. Nuclear sputtering and electronic sputtering occur due to completely different processes. Nuclear sputtering process has been carried out on number of materials and is well understood by Sigmund’s theory [2.8], whereas electronic sputtering is still in the way of indispensable research and desires considerable exploration for complete understanding. For multicomponent targets, the yield for each particular element should be taken into account. When the difference in Y among species in the substrate is large, a preferential sputtering of the target elements with greater Y occurs. This implies that the composition of the sputtered particles differs from that of the multi-component target and, as a consequence, induces an enrichment of the low-Y component at the outermost layers of the target. Although, there is no direct relation between the atomic number of the target element and the resulting Y, it has been reported that Y increases with ion fluence [2.12]. There are experimental observations on the behavior of Y as a function of other sputtering parameters; mainly ion flux, energy and incidence angle. An important experimental observation is that ion erosion occurs even in the limit of low ion flux and that Y is independent of the incoming flux. The variation of Y with the ion incidence angle (θ) which is measured with respect to
the surface normal, is considerable and increases from normal to oblique incidence until reaching a maximum around $60^\circ$-$70^\circ$, and then sharply dropping for glancing incidence angles [2.13]. The increase of $Y$ with $\theta$ is explained by the higher energy deposited in the surface region, a simple geometrical projection giving a $\cos^{-1}(\theta)$ relation. The reduction of $Y$ at glancing incidence is due to the increase in the reflection of the incident ions [2.14]. The variation of the sputtering yield with the angle (relation between the maximum sputtering yield and the value at normal incidence) depends strongly on the ion/target combination and will be larger for lighter targets.

The sputtering at low energy due to elastic collisions is called nuclear sputtering. This phenomenon is based on elastic energy transfer from ion to solid atom. Any ion striking on the solid matrix knocks out atoms due to a series of collisions in its journey. Knocked atoms may also remove other atoms due to secondary collisions from their lattice site. Therefore, a collision cascade develops inside the matrix. The energy is finally dissipated in displacements of atoms and in lattice vibrations. Surface or near surface atoms will be emitted if they receive a momentum in the direction to the vacuum with enough energy more than the surface binding energy. Low energy sputtering is also referred as nuclear sputtering. The schematic view of collision cascade is given in fig. 2.6.
Figure 2.6: Schematic of collision cascade resulting due to nuclear energy loss.

According to Sigmund’s theory [2.8], the sputter yield, \( Y \), can be given by:

\[
Y = \frac{0.42\alpha S_n}{NU}
\]  

(2.18)

where \( \alpha \) is a function of mass ratio of target and projectile, \( S_n \) the nuclear energy loss, \( N \) is the atomic density and \( U \) (in eV) is the surface binding energy of target material. The sputtering yield is directly proportional to the nuclear energy loss and has maxima at the peak value of \( S_n \) for a particular target and projectile combination. Sputtering has a lot of applications in different fields such as:

(i) **Deposition of thin films**: Thin films of a material can be deposited using sputter deposition. DC sputtering, RF sputtering, Magnetron sputtering, Reactive sputtering etc. are the well-known important deposition techniques based on sputtering.

(ii) **Patterning of surfaces**: Low energy sputtering is widely used for micromachining of the surfaces to produce desired surface topography.
(iii) **Sputter depth profile:** The controlled removal of material on an atomic scale from the surface by sputtering is the basis of many analytical techniques that aim to determine the sample composition as a function of depth. Secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) are well known examples of sputter depth profiler.

(iv) **Surface cleaning and thinning:** One other important application of sputtering is surface cleaning and thinning by removal of surface atoms.

### 2.2 THEORETICAL APPROACHES TO NANOPATTERNING (A Review)

The formation of nanostructures on the surfaces of various materials has been explained by many theoretical approaches. The first such approach was Bradley Harper equation which is based on the Sigmund’s theory of sputtering.

#### 2.2.1: SIGMUND’S THEORY OF SPUTTERING

According to Sigmund’s theory [2.15], assuming an infinite medium, in the elastic collision regime (at the energies of a few keV where electronic stopping is not dominating), the deposited energy can be approximated by a Gaussian distribution near its maximum. Specifically, the density of energy spread out in the bulk by an ion with kinetic energy \( E \) is given by

\[
\varepsilon_s(r') = EN_s e^{-\frac{x'^2+y'^2}{2\mu^2}} e^{-\frac{(x'+a)^2}{2\sigma^2}},
\]

where the origin of the \( r' = (x', y', z') \) coordinate system is placed at the impact point of the ion within the surface; \( z' \) is aligned along the ion beam direction, and \( \hat{x}' \) and \( \hat{y}' \) belong to the perpendicular plane to \( \hat{z}' \), see fig. 2.7. In Eq. (2.19), \( N_s = \left[(2\pi)^{3/2}\sigma\mu^2\right]^{-1} \) is a normalization constant and, due to the initial momentum of the ion, the maximum energy deposition occurs at a distance \( a \) along the ion trajectory inside the bulk, ‘a’ is called range of the ion. The longitudinal and transversal straggling widths of the distribution are \( \sigma \) and \( \mu \) respectively.
Figure 2.7: The 2-d profile of the distribution of energy deposition, where $\sigma$ and $\mu$ are the transversal and longitudinal widths of the Gaussian respectively.

The sputtering yield dependence on the surface topography plays an important role. Sigmund showed that the topography of the surface influences the magnitude of the rate of erosion. He provided an analytical description of the increase in yield for geometries different from the flat morphology [2.16]. It is assumed that the speed of erosion at a point $O$ on the surface is proportional to the amount of energy deposited there by the ions, with a proportionality constant $\Lambda$ which depends upon the substrate characteristics like atomic density of the target $n_v$ and the atomic binding energy $U_0$. The proportional constant $C_0$ is related to the square of the effective radius of the potential of effective interaction according to

$$\Lambda = \frac{3}{4\pi^2 n_v U_0 C_0}$$  \hspace{1cm} (2.20)

The mathematical expression for the rate of volume eroded in $O$ is given by

$$V_0 = \Lambda \int_R \phi(r') \varepsilon_s (r') dR$$  \hspace{1cm} (2.21)

The integral extends to the region $R$ where the impact of the ions contributes to energy deposition at $O$ and $\phi(r')$ is the local flux at $O$. Consider the irradiation of a certain surface with a homogenous flow of ions, as shown in fig. 2.8.
Figure 2.8: Schematic of the energy deposited for two different surface profiles. The energy deposited at O is larger than the energy deposited at O'. As a result the valleys eroded faster than the hill, which gives rise to morphological instability in the system.

As can be seen, the distances OA and OB are smaller than O'A' and O'B' due to the geometry of the interface. This implies that, for this energy distribution, the penetration of ions at C and D induce large energy deposition at O than the impacts on C' and D' at O'. As the rate of erosion is proportional to the deposited energy, erosion is faster at O than at O'. Thus, valleys are excavated more quickly than crests creating instability in the surface and amplifying initial differences in heights. Sigmund suggested that an alternative process that flattens the surface must exist and he proposed atomic migration as a mechanism to correct this instability.

2.2.2 BRADLEY-HARPER or B-H THEORY (LINEAR THEORY)

The theoretical description of the pattern formation on the surfaces due to the impact of energetic ions was given by Bradley and Harper (BH) in 1988 [2.17] which were based upon the Sigmund’s theory of sputtering [2.16]. It was predicted that the height \( h(x, y, t) \) of the eroded surface can be described by a linear equation:
\[
\frac{\partial h}{\partial t} = -v_o + v \nabla^2 h - D \nabla^4 h
\] 

(2.22)

where \(v_o\) is the constant erosion velocity, \(v\) is the effective surface tension and \(D\) denotes the surface diffusion which is activated by different physical processes (i.e. thermal diffusion, ion-induced diffusion) that may or may not involve lateral mass transport on the surface. The competition between the ion-induced surface instability and diffusive smoothening builds up a regular pattern on the surface with a characteristic wavelength. The negative sign indicates that the surface is getting removed or eroded. In general, the characteristic wavelength of the surface structure modulations is given by \(\lambda = \sqrt{\frac{2B}{v}}\). The linear model in eq. (2.22) predicts that the surface height grows exponentially with the time of irradiation or fluence and the wavelength is independent of fluence. The above model explained some of most basic experimental features of IBS ripple pattern formation on the surfaces but, it fails to explain the height evolution of the surfaces without any additional mechanism that will stabilizes the system. From eq. (2.22) one would expect the ripple wavelengths to be of the penetration length or range of the ion \(\alpha\), which is not the case, in experimental observations, ripple wavelengths are almost two orders of magnitude larger than \(\alpha\). In order to solve these problems, BH incorporates the last term in equation 2.2 to show the effects of the surface diffusion [2.18] for isotropic surfaces. This has stabilized the equation otherwise, the surface keeps on sputtering and the instability arises.

The orientation and wavelength of the observed ripple structures corresponds to the mode which maximizes, if:

(i) \(2\pi(2B/v_x)^{1/2}\) for \(v_x < v_y\), in this case the ripples orient along x direction,

(ii) \(2\pi(2B/v_y)^{1/2}\) for \(v_x > v_y\), in this case the ripples orient along y direction,

BH theory can’t predict the saturation of ripple amplitude and their non-uniform lateral motion as it doesn’t contain the second order terms.
If surface diffusion is thermally activated, as effectively occurs for high temperatures and small flux, the wavelength of the pattern with temperature, $T$ can be obtained. Since $D$ is given as:

$$D \sim \frac{1}{T} e^{(-\Delta E/k_B T)} \quad (2.23)$$

where $\Delta E$ is the energetic barrier to activate surface diffusion and $k_B$ is the Boltzman’s constant; wavelength $\lambda_l$ must verify,

$$\lambda_l \sim \left(\frac{1}{T^{1/2}}\right) e^{(-\Delta E/k_B T)} \quad (2.24)$$

So, the wavelength has no dependence on ion fluence. It is also possible to obtain a relationship between ripple wavelength and the kinetic energy and flux of ions, $E$ and $\phi_o$, respectively.

### 2.2.3 REFINEMENTS IN BRADLY AND HARPER THEORY (NON-LINEAR THEORIES)

There are certain refinements added to linear BH equation to explain the phenomena which were not explained by eq. (2.22). The refined theories include nonlinear effects with white noise coming due to the random arrival of the ions. Based on Sigmund’s continuum theory of ion-beam sputtering [2.16] Makeev, Cuerno and Barabasi (MCB) [2.19, 2.20] gave a model to describe the ion-induced pattern formation on amorphous or semiconductor materials that are easily amorphized by ion bombardment. The early stage morphology predicted by the MCB model [2.19] is similar to the linear instability theory developed by Bradley and Harper [2.17]. However, the late stage dynamics of the ion-induced morphology is dominated by the nonlinear terms of the Kuramoto-Sivashinsky (KS) equation [2.21] involved as described by Park et al. [2.22] and Rost and Krug [2.23]. Depending on the sign of the product of the coefficients of the two nonlinear terms, the late stage morphology may show kinetic roughening described by the universality class of the Kardar-Parisi-Zhang (KPZ) equation (2.25) or yield the formation of rotated ripple structure [2.8, 2.10] or display dots and hole
[2.25-2.27] on the ion eroded surface. Starting from the Bradley-Harper (BH) theory [2.17], description of the morphological evolution of ion sputtered surface can be given by the isotropic KS equation as [2.21, 2.23, 2.26, and 2.27]:

\[
\frac{\partial h(x,y)}{\partial t} = -\nu_o + \nu \nabla^2 h - D \nabla^4 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(x, y, t) \tag{2.25}
\]

where the nonlinear term $\frac{\lambda}{2} (\nabla h)^2$ is due to curvature dependent erosion yield that takes into accounts the saturation of surface roughness with time $t$, $\nu_o$ is the average erosion velocity of the surface during sputtering, $\nu$ is the effective surface tension induced by ion sputtering, $D$ is the coefficient related to relaxation by surface diffusion which comprises of thermal diffusion and ion induced diffusion, $\lambda$ is the tilt-dependent erosion rate, and $\eta(x, y, t)$ is white noise incorporating the stochastic nature of the ion-sputtering process mimicking the randomness resulting from the stochastic nature of ion arrival to the surface. KS model successfully explains most of the features of ion beam induced ripples, however, ripple coarsening with time and the short-range hexagonal ordering found in the nanostructures could not be explained [2.28].

2.2.4 SCALING THEORY

In the field of nanostructuring by ion beams, there are many developments in the theoretical aspects to describe the roughening of non-equilibrium surfaces and interfaces [2.29]. Due to the advances in the statistical mechanics of various non-equilibrium systems, it has been observed that the roughness of many natural surfaces follows simple scaling laws and can be quantified using scaling exponents [2.30, 2.31]. Since kinetic roughening is a common feature of ion bombarded surfaces, the scaling theories applicable to non-equilibrium film growth may also be applicable to ion bombarded surfaces [2.28]. Scaling theory is a theoretical tool to describe and characterize the roughening of non-equilibrium surfaces [2.29-2.32].
Considering a two-dimensional surface characterized by the height function, \( h(x,y,t) \).

The morphology and dynamics of a rough surface can be quantified by the interface width (W), defined by the rms fluctuations in the height \( h(x, y, t) \),

\[
W(L, t) \equiv \frac{1}{L^2} \sum_{x,y=1,L} [h(x,y,t) - \bar{h}(t)]^2, \quad (2.26)
\]

where \( L \) is the linear size of the sample and \( \bar{h} \) is the mean height of the surface defined as:

\[
\bar{h}(t) \equiv \frac{1}{L^2} \sum_{x,y=1,L} h(x,y,t) \quad (2.27)
\]

Instead of measuring the roughness of a surface over the whole sample size \( L \times L \), choosing a window of size \( 1 \times 1 \), where \( 1 < L \) and measure the local width, \( W(l) \). The roughness of a surface depends on the length scale which can be quantified by plotting \( W(l) \) as a function of \( l \). Two characteristic regimes can be defined:

(i) For length scales smaller than \( l_c \), \( (l << l_c) \), the local width increases as [2.29]:

\[
W(l) \sim l^\alpha \quad (2.28)
\]

where \( \alpha \) is the roughness exponent representing spatial evolution of the surface. To investigate the surface phenomena that take place at length scales shorter than \( l_c \), one cannot neglect the roughness of the surface. In this regime, the roughness is not simply a number, rather depends on the length scale of the measurement.

(ii) For length scales larger than \( l_c \), \( (l >> l_c) \), \( W(l) \) is independent of \( l \), thus at length scales larger than \( l_c \), one can characterize the surface roughness with the saturation width \( W_{sat} = W(l_c) \). The dynamics of the roughening process is given by Eqn. (1.14). At early times the total width increases as [2.29]:

\[
W(L, t) \sim t^\beta \quad (2.29)
\]

where \( \beta \) is the growth exponent representing time evolution of the surface.

However, for finite systems, after a crossover time \( t_c \), the width saturates, following the Family–Vicsek scaling function [2.32],.
\[ W(L, t) \equiv t^\beta f\left(\frac{t}{L^z}\right) \quad (2.30) \]

where \( z = \alpha/\beta \) is the dynamic or scaling exponent which gives the scaling and \( f(x) \) is a scaling function such that \( f(x) \) is constant for \( x \gg 1 \) and \( f(x) \sim x^\alpha \) for \( x \ll 1 \). Thus the roughness has the scaling property \( W(L, t) \sim t^\beta \) before saturation and \( W(L, t) \sim L^\alpha \) after saturation, \( \alpha \) and \( \beta \) are called roughness and growth exponents respectively. They characterize the nature of the surface roughness and growth and are independent of many details of the system in consideration [2.33, 2.34]. In contrast, other quantities, such as \( l_c \) or \( W_{\text{sat}} \), are non-universal, i.e. they depend on almost every detail of the system [2.35, 2.36]. The exponents, \( \alpha \) and \( \beta \), give spatial and temporal evolution of the structures, respectively and can be found out by plotting the power spectral density graph with the spatial frequency and plotting the rms roughness vs. fluence graphs extracted from the AFM images. The roughness parameter of the surfaces can be calculated from the slope \( n \) of the linear part of the PSD curves using the relation, \( \alpha = (n-d)/2 \), where \( d \) is the dimensionality of the PSD taken which is 2 for our case.

The power spectral density (PSD) of the sample surface is the square of the magnitude of the Fourier transform of the surface profile. PSD can provide quantitative information about the surface roughness in both the vertical and lateral directions and is independent of the scan size. The 2D PSD function is defined as

\[ \text{PSD}(y) = \frac{1}{\text{area}} \left[ \int \frac{d^2 r}{2\pi} e^{-iqr} < h(r) \right]^2 \quad (2.31) \]

where \( r = r(x,y) \), \( q \) is the spatial frequency (nm\(^{-1}\)) and \( h(r) \) is the surface height at a point \( r \) [2.36]. The scan sizes of 2\( \mu \text{m} \times 2\mu\text{m} \) and 512 \( \times \) 512 data points have been used to scan the samples in AFM. Eklund et al. [2.37] have reported the value of \( \alpha = 0.2-0.4 \) which is consistent with the predictions of the Kardar-Parisi-Zhang equation. It is reasonably in good agreement for ion induced roughening with the exponent for growth without surface diffusion. In scaling studies for non-equilibrium film growth by deposition, value of \( \alpha = 0.35 \).
[2.38] is expected when surface mobility of deposited particles is not allowed. The value of $\beta$ can be found out by plotting the rms roughness versus ion fluence in the log plot and is found to lie between 0 and 1. The high value of $\beta$ indicates exponential increase in the surface roughness. For lower fluences, the roughness increases exponentially and for higher fluences the surface roughness attains a saturation value [2.39, 2.40].