1 Introduction

This chapter is divided into six sections: (i) Passage of energetic ions through matter, (ii) sputtering: an effect of ion-solid interaction, (iii) motivation behind the study of electronic sputtering, (iii) materials under study for electronic sputtering and motivation, (iv) experimental techniques to measure electronic sputtering and (vi) existing theoretical models.

1.1 Passage of energetic ions through matter

Ion-matter interaction occupies an important portion of 20th Century Physics. The endeavor receives a spectacular growth after the discovery of accelerators of different energy ranges. During the passage through matter, ions interact with material by two-processes: (i) with the atoms of the lattice and (ii) with atomic electrons. The strength of interaction depends on incident ion mass and its energy. The first one (i.e. interaction with atomic nuclei) is an elastic collision process between lattice atoms and incident ions, which is prominent at low energy (eV to few hundred keV). The second one (i.e. interaction with electrons) is the inelastic
collision of incident ions with electronic subsystem of material and is prominent at
higher energies (a few tens of MeV and higher) regime. The first energy loss
process is termed as nuclear stopping, designated by $S_n$, and the second one is
electronic stopping, designated by $S_e$. Nuclear stopping is understood as a two-body
central force scattering problem in a complex interatomic potential. Electronic
stopping is understood entirely as an inelastic collision between incident ion and
target electrons within the framework of local density approximation. The nuclear
energy loss, $(dE/dx)_n$ or $S_n$ is given by the mathematical equation [1]:

$$
\left[ \frac{dE}{dx} \right]_n = \frac{N \pi^2 Z_1 Z_2 e^4 a M_1}{2(M_1 + M_2)}
$$

(1.1)

where, $N$ is the number of atoms/cm$^3$ in the solid, $Z_1$, $Z_2$, $M_1$ and $M_2$ are atomic
numbers and masses of incident ion and target atoms respectively and $a$ is the
screening radius for collision.

Mathematical equation for electronic energy loss, $(dE/dx)_e$ or $S_e$ is given by Bragg’s
law [2]:

$$
\left[ \frac{dE}{dx} \right]_e = \frac{2 \pi Z_1^2 e^4}{E} . N Z_2 \left( \frac{M_1}{m} \right) \ln \frac{2mv^2}{I}
$$

(1.2)

where, $m$ is the mass of electron, $v$ is the velocity of the incident ion and $I$ is the
average ionization potential of electron.
Detailed mathematical work on energy loss processes is furnished by Ziegler and Biersack [3] and a computer simulation program, Transport of Ions in Matter (TRIM) has been developed. Based on this simulation program, the following calculations are done to obtain an idea how the nuclear energy loss and electronic energy loss vary with incident ion energy and depth inside a solid:

(i) $S_n$ and $S_e$ of Ni, Ag and Au of energy 100 eV to 1 GeV in carbon (figure 1.1).

(ii) $S_n$ and $S_e$ versus depth for Ni, Ag and Au ion (of 1 GeV energy) in carbon (figure 1.2).

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Figure 1.1: $S_n$ and $S_e$ versus energy for Ni, Ag and Au ion in carbon
Figure 1.2: Stopping power \( S_n \) and \( S_e \) versus depth for Ni, Ag and Au ion in carbon

From these figures, the following salient points of ion-matter interaction are clear:

(i) Nuclear energy loss is dominant at lower energies, whereas electronic energy loss is dominant at higher energies, (ii) the peak of electronic energy loss, known as Bragg peak (as indicated in figure 1.1) shifts to higher energy side for heavier incident ions, (iii) the peak corresponding to electronic energy loss is always higher (two orders and magnitude and more) than that of the nuclear energy
loss, (iv) nuclear energy loss peak appears at a higher depth and (v) the value of $S_e$ is almost constant for a film of thickness up to a few micrometer (as shown in figure 1.2).

Next section is based on how these energy losses cause the ejection of atomic species from the solid, known as sputtering.

1.2 Sputtering: an effect of ion solid interaction

Several fascinating phenomena take place due to the energy deposition of ions in the solids. Sputtering is one among these. This is defined as removal of material from the surface of a solid due to the impact of energetic particles. The material released from the bombarded solid consists predominantly of single atoms and sometimes-sizable fraction of homo- or heteronuclear clusters. The ejected particles have a broad energy and angular distributions. The mean energy of sputtered particles is of the order of 10 eV. Generally any energetic radiation such as ions, neutral atoms, neutrons, electrons or photons that causes damage in the bulk of a solid will also causes sputtering. The process of sputtering has applications in various fields. Some of these applications will be highlighted in the next part of this section.

As far as the sputtering of any solid by heavy ion is concerned, there are two distinct regimes. First one is the low energy (eV to a few hundred keV) sputtering influenced by nuclear energy loss and the second one is the high energy (tens of MeV) sputtering mediated by electronic energy loss. Second one is defined as
electronic sputtering [4]. The demarcation of these two phenomena is demonstrated (oxygen ion on ice) by R. E. Johnson et al. [5] and depicted in figure 1.3.

![Figure 1.3: (a) $S_n$ and $S_e$ versus ion energy. (b) Collisional sputtering and electronic sputtering versus square of the ion velocity.](image)

In fig. 1.3(a), $S_e$ and $S_n$ are plotted with respect to incident ion energy. In fig. 1.3(b), the sputtering yield is shown with respect to energy. This indicates very clearly that a high sputtering takes place beyond the energies corresponding to the
maximum nuclear energy loss and is governed by the electronic energy loss only. Low energy sputtering and electronic sputtering are phenomenologically completely different processes. Low energy sputtering is quite well understood and has lot of applications. Electronic sputtering is still in the way of fundamental research and requires several investigations to have a complete understanding.

1.2.1 Low energy sputtering

This process is based on elastic energy transfer from ion to solid atom. A pictorial representation of this sputtering is given in figure 1.4.

Figure 1.4: Pictorial representation of collision cascade and low energy sputtering
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Any ion impinging on the solid matrix knocks out atoms due to series of collisions in its journey. Knocked out atoms may also remove other atoms from their lattice sites due to secondary collisions. Thus a collision cascade develops inside the matrix. 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. Sputtering has, therefore analogy with "atomic pool" where the ion (cue ball) breaks up the closed packed rows of atoms (billiard balls), some of these scatter in back direction (towards the player) [6]. Generally more than 60% of the ejected atoms originate from the first atomic layer, while the remaining originate from the layers underneath [7]. Low energy sputtering is an athermal process, with a major fraction of the lattice atoms staying cold during the initial spread of the cascade that leads to sputtering. The energy is finally dissipated in displacements of atoms and in lattice vibrations. The collision cascade evolution is influenced by the crystal lattice structure [8,9]. Low energy sputtering is referred as nuclear sputtering or conventional sputtering.

1.2.1.1 Sputtering yield

The most important and widely investigated quantity [7] for describing the sputtering process is the sputtering yield $Y$, which is defined as the average number of atoms released from the solid’s surface per incident particle. Commonly, sputtering is accomplished using energetic ions or neutral atoms. When sputtering
is initiated by bombardment with energetic electrons or photons [10] or with neutrons [11] the same definition of the sputtering yield can be applied. Detailed mathematical formalism of low energy sputtering yield is done by Sigmund [6] using the idea of elastic binary collision same as billiard balls even though the atoms of a solid is bound to one another by a complex interatomic potential, whereas billiard balls do not interact. Generally, the sputtering yield can be described by two terms: one describes the density of the energy deposited by the incident particle leading to motion of the target atoms near surface, and the other, a material factor containing the atomic density and the surface binding energy of the solid. The sputtering yield obtained from this theoretical calculation is,

$$Y = \frac{0.042\alpha S_n}{NU}$$

Where $Y$ is the sputtering yield, $\alpha$ is a function of mass ratio of target and projectile and generally ranges between 0.2 to 0.4 [1], $S_n$ the nuclear energy loss, $N$ is the atomic density and $U$ (in eV) is the surface binding energy. It is evident from the equation (1.3) that sputtering yield is directly proportional to nuclear energy loss. For same solid and ion combination, sputtering yield ($Y$) becomes maximum at the peak value of $S_n$. $Y$ falls down after this peak value at higher energies as shown in figure 1.3. At higher energy the decrease in sputtering yield is due to the fact that the nuclear energy loss decreases with increase in energy after the energy
corresponding to the maxima of $S_n$. Low energy sputtering process received immense applications such as:

(i) **Sputter depth profile:** The controlled removal of material on an atomic scale from the surface of solids by sputtering is the basis of many current analytical techniques that aim at determining the sample’s composition as a function of depth (sputter depth profiling).

Examples of this are Secondary ion mass spectrometry (SIMS), Auger electron spectroscopy (AES) etc.

(ii) **Micromachining:** Low energy sputtering widely used for micromachining of the surface i.e. to produce desired surface topography.

(iii) **Sputter deposition:** Another technologically and commercially important application of sputtering is the controlled deposition of sputtered material on substrates of almost any conceivable composition and geometry in film deposition. DC sputtering, RF sputtering, Magnetron sputtering, Reactive sputtering etc. are the important sputter deposition techniques.

(iv) One important use of low energy sputtering is to remove material from surface for surface cleaning and thinning.

### 1.2.2 High energy sputtering (electronic sputtering)

When the incident ion energy is high, the elastic collision probability drops down and hence the nuclear sputtering yield also reduces as shown in figure 1.3.
However, it has been observed that high erosion of the material takes place (figure 1.3) when incident ion energy crosses a particular threshold of energy deposition. This threshold depends on ion as well as material. In this energy regime, electronic energy loss \( (S_e) \) dominates over collisional loss and hence the sputtering or erosion process is mediated by electronic energy loss. This erosion process is defined as electronic sputtering [4] as indicated earlier. The electronic sputtering is observed in insulators [12,13], condensed gases [14,15], bio-polymers [16,17] and metals [18,19]. Particularly in case of insulating materials, the yield is found to be quite high. Erosion of materials from the surface of solids (surface erosion) and evolution of light and gaseous species all along the ion damage path (desorption) due to electronic energy deposition both comes under the electronic sputtering process. Electronic sputtering is not as clearly understood as nuclear sputtering. Haff first suggested that [20] the mechanism for latent track formation and electronic sputtering should be similar. Since then, different theoretical formalisms are proposed (sec. 1.6), still complete understanding of the electronic sputtering mechanism is yet to be achieved. The energy coupling from electrons to lattice is a complicated process and depends on many parameters related to the solid. Investigations are in progress to find what factors are playing the desciscive role behind this phenomenon. A pictorial representation of electronic sputtering process up to the present understanding is depicted in figure 1.5. This represents that the erosion basically takes place from a confined ion effected zone.
1.3 Motivation behind the study of electronic sputtering

Electronic sputtering is an important tool to understand the swift heavy ion (SHI) -solid interaction. Particularly the quantification of electronic sputtering yield can shed light on the interaction process that takes place between SHI and solid lattice through electronic excitation and ionization. The present work is aimed to study electronic sputtering of thin films in order to understand the interaction mechanism. Following aspects of electronic sputtering are investigated.

1.3.1 Dependence of electronic sputtering on $S_e$

Since the discovery of electronic sputtering phenomenon, dependence of electronic sputtering yield (atoms/ion) on the electronic energy loss ($\left(\frac{dE}{dx}\right)_e$ or $S_e$) is a subject of extensive research [21-23]. The process depends on the way energy is
distributed in the lattice subsystem. It is seen [23] that for higher electronic energy density, the yield has a non-linear dependence on $S_e$. In order to understand electronic sputtering phenomenon, two schools of thoughts [24-26] emerged based on "ionic spike" [24] and "thermal spike" processes [25,26]. Among these two mechanisms, thermal spike approach is often used in this regime due to its conceptual simplicity and mathematical tractability. Standard spike models predict roughly a quadratic dependence with the energy deposited per unit path length ($S_e$) for high-energy regime [25,27]. On the other hand, molecular dynamics (MD) studies [28] however, showed that the predicted quadratic dependence might not always be true. In case of frozen Ar and O$_2$, the sputtering yield appeared to be close to a linear function of dE/dx. Recently, it has been shown [29] that the prediction based on thermal spike model becomes more realistic if the pressure pulse arising due to large local temperature rise is considered. This pressure pulse can carry away a fraction of energy and this can influence the sputtering yield. As the pressure pulse carries away energy from the core, the sputtering yield decreases and the quadratic dependence does not hold good. Therefore, a systematic study on electronic sputtering corresponding to different electronic excitation and its comparison with theoretical prediction will give information on interaction process. The motivation of the present work is to investigate the dependence of electronic sputtering yield on $S_e$ and the basic physical process involved in this phenomenon.
1.3.2 Dependence of electronic sputtering on microstructure

It is known that the sputtering yield of fine grain material is considerably large as compared to the same material having larger grains [30]. This is one of the important characteristic features of electronic sputtering [31,32]. The first direct investigations of the dependence of electronic sputtering process on the structure of a solid were carried out on gold samples [33]. It was found that the sputtering yield of fine-grained gold films bombarded with $^{252}$Cf fission fragments was $\sim 10^3$ atoms/fragment, whereas for the gold foil it was $\sim 10$ atoms/fragment [33]. In case of metal oxides (UO$_2$, AmO$_2$ etc.) fine grained samples were found to have a sputtering yield $\sim 10^2$ atoms/fragment [34,35], whereas coarse grained samples had an yield $\sim 10$ atoms/fragment. These studies are first indications of structural dependence on electronic sputtering. However, the ion used in these studies is a $^{252}$Cf fission fragment source, which has a broad energy distribution. It was therefore a natural question to observe the influence of solid structure on electronic sputtering induced by monoenergetic heavy ions. Furthermore, the physical process behind electronic sputtering dependence on microstructure is yet to be understood. Large erosion of amorphous carbon films was observed by Behrisch et al. [36] ($\geq 10^5$ atoms/ion) and by Pawlak et. al. [37] ($\sim 10^4$ atoms /ion). The sputtering rate measured in these two works have an order of magnitude mismatch for the same electronic excitation ($S_e$) value. The mismatch in electronic
sputtering of a-C:H films despite of similar electronic energy loss indicates that the energy transfer from ion to the lattice must depend on certain factors related to the structure of the films. One of the objectives of the present work is to study sputtering dependence on microstructure.

1.3.3 Dependence of electronic sputtering on allotropic phases

Different solid state phases of a same element is known as the allotropes of that element. The study of electronic sputtering of different solid phases having wide variation in structure and property (of a particular material) is a unique investigation for the understanding of the sputtering phenomenon. Aiming at this point, we have chosen carbon allotropes, which have a significant variation of structure and physical properties.

1.3.4 Dependence of electronic sputtering on film thickness

The study of electronic sputtering of thin films having different thickness could be an important parameter to understand SHI-solid interaction [38]. The main physical process involved in this is the energy confinement in the films, which is dependent on film thickness. There is apparently no study to measure the electronic sputtering yield from the films of different thickness. The motivation behind the present work is to understand the influence of thickness (i) on the energy confinement inside the material and (ii) on the electronic sputtering yield.
1.3.5 Dependence of electronic sputtering on the substrate

In case of very thin film, substrate can play an important role in the energy distribution in the lattice of the film due to ion bombardment. The electrical and thermal energy generated due to passage of ion in the substrate will try to smear out faster across the film and substrate interface if the substrate has a poor conductivity (electrical as well as thermal). This will influence the confinement of energy in the film and hence the sputtering yield. The electronic sputtering study of a thin film deposited on different substrate will give an idea about the role of substrate in energy transfer process. One of the objectives of the present work is to look into the substrate dependence.

1.3.6 Dependence of electronic sputtering on incident ion velocity

For swift heavy ion irradiation, it is now clear that the incident ion looses the main part of its energy by interactions with electrons. From the study of energy density deposited in water by the secondary electrons generated inside the ion path in different directions, Waligorsky et al. [39] have discussed the radial distribution of deposited energy. The radial distribution depends on ion energy. Incident ions having different velocities but having similar $S_e$ on any solid have different radial energy distribution. The energy density, in case of slower ion will be higher as compared to faster ion. This give rises a distinct difference in damage creation [40]. Up to now the velocity effect is seen in track formation and discussed on the basis
of radial energy distribution and in the framework of thermal spike model. Whether this has an impact on electronic sputtering yield has not been investigated so far. Therefore, study on the influence of incident ion velocity on the electronic sputtering is undertaken here to see the velocity effect.

1.4 Materials under study for electronic sputtering and motivation

Two types of materials are selected for electronic sputtering study: (i) allotropes of carbon (amorphous carbon, hydrogenated amorphous carbon, fullerene, graphite and diamond), (ii) Inorganic compound materials. In the second type, thin films of copper nitride, copper oxide and silicon di-oxide are selected. In this section all these materials will be described briefly and then the motivation behind selection of these materials will be addressed.

1.4.1 Allotropes of carbon

Carbon, a wonder material in the periodic table, has different structural varieties. It is one of the most suitable materials to study the structural effect on electronic sputtering yield. The complex atomic hybridization in the lattice network of carbon gives rise to very hard structural phase as well as to very soft material. The motivation behind selecting this material for electronic sputtering study is to see how a same element in the periodic table having different structural phases responds to swift heavy ion. Depending on the bonding nature of carbon atoms, there are several allotropes, which are described briefly:
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(i) Diamond: This is one of the crystalline forms, a classic example of strong $sp^3$ tetrahedral bond of carbon atoms. Diamond is one of the hardest materials known with high electrical resistivity and thermal conductivity. The very special structure of diamond attracts lot of interest in ion interaction research [41,42].

(ii) Graphite: This is another crystalline form of carbon with hexagonal layer by layer structure. In plane layers, C atoms have strong $sp^2$ bonded carbon atoms. Out of plane carbon atoms are bonded by weak Van der Waal’s force.

(iii) Fullerene ($C_{60}$): This is the third crystalline allotropic form of carbon having a truncated icosehedral symmetry. It is a combination of hexagon and pentagonal structure where carbon atoms are hybridized as both $sp^2$ and $sp^3$ bonds.

(iv) Amorphous carbon (a-C): This is amorphous form of carbon having different hybridized bonds ($sp^1$, $sp^2$ and $sp^3$). This itself is a class of material having different structural variety. The structural variation becomes more versatile if hydrogen gets incorporated in the network. If hydrogen percentage is high, different $sp^3$ bonds ($C(sp^3)$-H) consisting of carbon and H ($CH_x$) are formed which make the network polymerlike. If the H content is less, the material is likely to be more diamond like. Our interest of study is hydrogenated amorphous carbon (a-C:H) and a-C films. In the former case hydrogen is incorporated deliberately during the deposition process, whereas in the latter case no H is introduced during growth. This makes a structural difference of theses two allotropes.
1.4.2 Copper Nitrides

Among different compound films, nitrides, which are receiving great attention in different field of research, is rarely studied under swift heavy ion irradiation. Among different nitrides, covalent binary nitride films are receiving great attention due to their emerging applications [43]. One of the important characteristics of these materials is their volatile nature after some hundreds of Kelvin temperature. The release of the constituents of nitride films due to ion impact can be of significant importance to study the thermal effect induced by ion. In the present study, we have chosen copper nitride film. The reasons behind selecting this material are: (i) it is easy to vary the crystallite size of this film only by changing substrate temperature [43], which can be studied in terms of crystallite size effect on electronic sputtering, (ii) it starts decomposing at 600 K and hence the erosion of its constituents can be of importance in order to understand the thermal energy rise in the solid due to SHI irradiation.

1.4.3 Oxides

Presently oxide materials are receiving great attention as far as the swift heavy ion induced effects are concerned [44,45]. It is seen that oxides are prone to latent track formation [44] and electronic sputtering too. The dependence of electronic sputtering of oxides with $S_e$ is a topic of interest for understanding regarding ion solid interaction [45]. In this work we have selected two oxides, copper oxide (CuO) and silicon dioxide (SiO$_2$).
1.5 Experimental techniques to measure electronic sputtering

Several experimental techniques have been devised to study electronic sputtering. One of these methods is to collect the sputtered species and their quantitative analysis. Another method deals with measuring the content left after electronic sputtering. Two typical examples of the first method is time of flight (TOF) and catcher technique. In the second method, the material undergoing electronic sputtering can be analyzed off-line as well as on-line. Sputtered species can be quantified by Rutherford backscattering (RBS), Secondary ion mass spectroscopy (SIMS), X-ray reflectivity (XRR) etc. In on-line method, ERDA is the suitable technique to quantify sputtering yield. Here these three techniques are described briefly and the justification is given why on-line ERDA is chosen for the most of the cases in present study. Only in one particular case the catcher technique is used and the reason behind this is outlined.

1.5.1 Time of flight (TOF)

In this technique, two timing detectors (start and stop) separated by a distance \( l \) gives the elapsed time \( t = t_2-t_1 \) taken by the sputtered ion. If the velocity of the ion is \( v \) and energy is \( E \) we can write,

\[
M = 2E\lambda^2 = 2E \frac{I_2}{I_1}
\]  

(1.4)
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This is of course in the non-relativistic assumption, which is satisfied in the majority of the cases studied. From the above equation, we see that mass is proportional to \( t^2 \). Any unknown mass can be identified with respect to a known mass (generally H) using this mass and time relationship. Number of sputtered particles are obtained from the TOF spectrum. Though this technique is suitable for particle identification, there are some demerits as far as the electronic sputtering study is concerned: (i) when single ion produces large number of sputtered species electronics of the set-up becomes very much complex (ii) detecting neutral species is not possible.

1.5.2 Catcher technique

This is a rather simple technique where sputtered species are collected in a catcher (e.g. small piece from Si wafer) placed as close as possible to the sample. Sputtered material get deposited on the catcher, which is analyzed by RBS, ERDA etc. techniques. The problems involved in this technique are (i) dummy catcher has to be made and it should undergo all the physical conditions as the actual one, (ii) vacuum has to be broken in order to get the catcher for analysis.

1.5.3 On-line ERDA technique

In this technique, a higher mass projectile is used to generate recoil atom (of lower mass compared to projectile ion) from the target. These recoils are detected in a
forward geometry for a fixed number of incident ions. From the integral counts of the recoils and the number of incident ions, the content (in atoms/cm$^2$) of any element is determined. In case of electronic sputtering of an elemental species, the content of this particular element goes down, which can be measured on-line, at different ion fluences. This is applicable to thin films only. The details of this technique is described in chapter 3.

Due to the following advantages, we adopt this technique for our study: (i) suitable for thin films, (ii) recoils generated due to the impact of heavy ions (Au, I, Ag) with high energy (100 to 200 MeV), have energies well above the Bragg peak and can be better identified with suitable detection system (iii) sputtering yield calculation takes care sputtered ions as well as neutrals also (iv) ERDA with large solid angle telescope detector makes the technique quite sensitive for the detection of different elements (v) on-line study avoids the probability of contaminating the sample due to vacuum break.

In the present thesis work, on-line ERDA is employed to measure electronic sputtering yield from all the thin films. Catcher technique is used for bulk graphite sample. A suitable detection technique is designed, fabricated and installed in house for this study.

1.6 Existing theoretical models

According to the discussion of section 1.1, it is now clear that SHI deposits most of its energy to the electrons of the target material.
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The question arises what are the subsequent processes that provide enough kinetic energy to the atoms to escape from the material. There are several theoretical approaches to understand the electronic sputtering process. The first goal of all these approaches is to explore the fundamental of MeV ion-matter interaction and to find the possible reason behind latent track (a nanometer size cylindrical (approximately) damaged zone created around the ion path) formation. Later these theories were developed to explain more complicated processes like electronic sputtering, interface mixing etc. However, each model has its own limitations in complete explanation of electronic sputtering. In order to have feeling of the electronic sputtering phenomenon in the light of different theoretical models, a brief description of the models are given below:

1.6.1 The varying electric field model

Krueger [46] first developed this model. Ionization caused by a fast heavy ion creates a time varying electric field (~5 V/Å). This is sufficient in itself to lift the molecules into unbound states. Main drawback of this model is that it cannot predict the dependence of sputtering yield on the electronic stopping power.

1.6.2 The Ion track model

In this model [47], the number of excitations of a molecule by secondary electrons are evaluated. These electron "hit" can lead to the bond breaking of molecules and its neighbors. Desorption occurs when the number of hits exceeds a critical value
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depending on the size of the molecule. Yield is related to the local electron flux at the surface and the critical hit number. This model does not describe the ejection process itself.

1.6.3 Sum of impulse model

R. E. Johnson et al. proposed this model [48] and tried to scale sputtering yield with $S_e$. According to this model, the energy deposited by fast heavy ions create a cylindrical track of energized material in the surface region. The resulting molecular motion causes the material to expand against the surrounding unexcited material. This model describes the ejection as a result of this expansion. It is due to contribution from radial impulses all along the track. At low excitation density, these impulses act independently. On the other hand, at high excitation density these impulses overlap contribute cooperatively [48]. This is of course, an approximation invoked in this work to describe sputtering yield at high excitation densities. Therefore, at low $dE/dx$, ejection of tightly bound species will depend on the statistical occurrences of a number of closely spaced events, resulting in a rapid dependence of the yield on $dE/dx$. Increasing, $dE/dx$, the impulse will eventually act cooperatively to eject large species or to cause additional ejection of small species. For large species, the volume ejection mechanism dominates. That is at a very high $dE/dx$, the impulses act cooperatively forming a pressure pulse which gives an overall outward and radial momentum to a volume of material at the surface. This has been treated as a shock phenomenon. For the lineraized pressure
pulse with a cylindrical geometry, the yield scales as \((dE/dx)^3\). In figures 1.6(a) and (b), the impulse generated at low and high excitations are represented.

Figure 1.6: Track of impulses: (a) vectors indicate the expansion around track of ion along \(z\) direction, \(r\) is the radial distance from ion path, (b) summing up of impulses at high excitation densities.

However, the generation of such excited and impulsed regions and their cooperation, depends completely on the charge neutralization time of the material under consideration. In case of metals and some insulators viz. a-C, the neutralization is quite fast and hence the formation of impulse cannot be conceived. This model could explain the ejection of large molecules from biomaterials but not be applicable in general.
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The two most popular theories up to recent times, which explain the basic interaction mechanisms between SHI and solid, damage zone formation and electronic sputtering are the electrostatic [24] and thermal models [25,26].

1.6.4 Electrostatic model

In this model [24], it is considered that when a heavy ion passes through a material, it ionizes adjacent atoms along the path. The rate of such ionization per unit path length is denoted by $dJ/dx$ and is first calculated by Bethe, which is

$$
\frac{dJ}{dx} = \frac{AZ_{eq}^2 \ln(BE_m)}{E_m}
$$

where $A$ and $B$ are constant depend on the incident ion and target material, $E_m$ is the ion energy per atomic mass unit, and $Z_{eq}$ is the equilibrated charge of the ion. The highly ionized matter along the ion path explodes due to electrostatic repulsion before its neutralization. The neutralization depends on the mobility of the excited electrons. The electrostatic energy converts into the kinetic energy of the lattice atoms. This atomic motion can cause a low energy collision cascade [20], which eventually leads to sputtering. The problem often discussed in this model is, the conversion of electrostatic energy to the kinetic energy if the electron return time to the ion core $\geq 10^{-13}$ sec [21]. Whether such electron return time is realized is in question. Hole mobility must also be considered. Moreover, the enhancement
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of electron mobility which one must expect in the highly excited region has apparently been neglected in this model. A second reason that hinders the explosion is the screening of the ions by electrons due to the high field strength and corresponding polarization. In figure 1.7, the schematic view of ionized explosion is represented.

Figure 1.7: Pictorial representation of ionization and explosion.
In order to get rid of some of the problems in this model, a molecular expansion model has been proposed [21]. The basic assumption of this model is that, an excited molecule expands and develops a pressure onto the boundaries of a lattice cell or a molecule in a solid. The Fermi pressure [21] of an excited electron gas confined to a Wigner-Seitz cell provides the force acting on atoms. Here, the repulsive Coulomb force of the charge-separated core does not cause the motion of the atoms. Essential for the sputter yield is, how fast the excitation energy is conducted away via electron-electron collisions as compared with the time needed to put an atom in motion.

1.6.5 Thermal spike model

This model [25,26,49] considers (first approach) the overall interaction in two steps: in the first step the energy deposited by incident ion gets shared in the electronic subsystem which cause a rapid (~10^{-15} sec) temperature spike in the subsystem. Eventually, the electronic subsystem comes into thermal equilibrium with the lattice atoms via electron phonon coupling. The thermal energy transfer from electronic subsystem to the lattice subsystem governs by two differential equations in cylindrical geometry:

\[ C_e \frac{\partial T_e}{\partial t} = \nabla (K_e \nabla T_e) - g(T_e - T) + B(r,t) \]

\[ \rho C(T) \frac{\partial T}{\partial t} = \nabla (K(T)\nabla T) + g(T_e - T) \]  

(1.6)
where $T_r, T, C_r, C(T), K_e$ and $K(T)$ are the temperature, the specific heat and thermal conductivity of the electronic and atomic systems respectively and $g$ is the electron-phonon coupling strength. Duration of temperature spike in the lattice is about ten to hundred picosecond [50]. The pictorial representation of temperature spike developed in SiO$_2$ [45] based on this theoretical calculations is shown in figure 1.8.

![Figure 1.8: Thermal spike in SiO$_2$ (from [45]).](image-url)
Another approach [29] considers that only a fraction of the total deposited energy initially contributes to the thermal spike. This temperature rise is governed by the following equation:

$$E_{exc} = \int_{0}^{\tau_{exc}} C_v(T) dT$$

(1.7)

where, $E_{exc}$ is the fraction of total deposited energy and $C(T)$ is the specific heat.

Whatever be the reason behind the thermal spike in the lattice, both the approaches consider that the thermal spike cools very rapidly in the lattice medium due to conduction. Electronic sputtering is likely to take place in the thermal spike duration. Temperature evolved in a cylindrical geometry and the ejection of materials takes place from this hot cylinder [29]. This may be associated with a pressure pulse [29] depending on the medium and temperature, which carries away energy from the track. Though realistic estimations of electronic sputtering yield is obtained from spike models, the main problem with the calculation is the thermodynamical parameters viz. specific heat, thermal conductivity etc. in the highly excited and thermalized ion track which again depend on microstructure and crystallinity of a material.

Concerning all the theoretical understandings related to the ion-matter interaction, it is a daunting task for experimentalists to provide enough data for different ion-
material combinations, considering all the physical parameters related to material as well as ions. The present work, which provides several experimental data on electronic sputtering, is a step in this direction.

The next chapters of the thesis are arranged in the following manner.

In chapter 2, the preparation of the samples by different thin film deposition techniques is described.

Chapter 3 deals with the overall experimentation (on-line and off-line) of this work. This chapter starts with the principle of elastic recoil detection analysis (ERDA) technique followed by the utility of telescope detector in ERDA studies and on-line experiments. The last part of this chapter describes the details of off-line experiments, which contains grazing angle x-ray diffraction (GAXRD), atomic force microscopy (AFM), Raman spectroscopy and optical spectroscopy.

In chapter 4, the results on different characterization of the samples are given. Basically, this chapter makes us familiar about crystallinity, surface morphology, microstructure, band gap, thickness and stoichiometry of the films.

Chapter 5 is the most important part of the present work. It has discussion on the results of all on-line electronic sputtering studies and the possible explanation in the framework of SHI-solid interaction process.

Chapter 6 concludes the work with comments on the future prospects.
Chapter 1: Introduction

Bibliography

2. M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. 9 (1937) 261.
Chapter 1: Introduction

Chapter I: Introduction


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