SPUTTERING OF Bi AND PREFERENTIAL SPUTTERING OF AN INHOMOGENEOUS ALLOY

Naresh T. Deoli

Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

December 2014

APPROVED:

Duncan L. Weathers, Major Professor
Samuel L. Matteson, Committee Member
Bibhudutta Rout, Committee Member
Floyd D. McDaniel, Committee Member
Chris L. Littler, Chair of Department of Physics
Mark Wardell, Dean of the Toulouse Graduate School
Angular distributions and total yields of atoms sputtered from bismuth targets by normally incident 10 keV - 50 keV Ne\(^+\) and Ar\(^+\) ions have been measured both experimentally and by computer simulation. Polycrystalline Bi targets were used for experimental measurements. The sputtered atoms were collected on high purity aluminum foils under ultra-high vacuum conditions, and were subsequently analyzed using Rutherford backscattering spectroscopy. The Monte-Carlo based SRIM code was employed to simulate angular distributions of sputtered Bi atoms and total sputtering yields of Bi to compare with experiment. The measured sputtering yields were found to increase with increasing projectile energy for normally incident 10 keV - 50 keV Ne\(^+\) and Ar\(^+\) ions. The shapes of the angular distributions of sputtered Bi atoms demonstrated good agreement between experiment and simulation in the present study. The measured and simulated angular distributions of sputtered Bi exhibited an over-cosine tendency. The measured value of the degree of this over-cosine nature was observed to increase with increasing incident Ne\(^+\) ion energy, but was not strongly dependent on incident Ar\(^+\) ion energy.

The differential angular sputtering yield and partial sputtering yields due to Ar ion bombardment of an inhomogeneous liquid Bi:Ga alloy have been investigated, both experimentally and by computer simulation. Normally incident 25 keV and 50 keV beams of Ar\(^+\) were used to sputter a target of 99.8 at\% Ga and 0.2 at\% Bi held at 40\(^\circ\) C in ultra-high vacuum (UHV), under which conditions the alloy is known to exhibit
extreme Gibbsian surface segregation that produces essentially a monolayer of Bi atop the bulk liquid. Angular distributions of sputtered neutrals and partial sputtering yields obtained from the conversion of areal densities of Bi and Ga atoms on collector foils were determined. The Monte-Carlo based SRIM code was employed to simulate the experiment and obtain the angular distribution of sputtered components. The angular distribution of sputtered Ga atoms, originating from underneath the surface monolayer, was measured to be sharply peaked in angle about the surface normal direction compared to the Bi atoms originating from surface monolayer. The simulation study produced contradicting results, where the species originating from surface monolayer was strongly peaked around the surface normal compared to the species originating from beneath the surface monolayer.
Copyright 2014

by

Naresh T. Deoli
ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Duncan Weathers, as without his help and support this work would have been impossible. His encouragement and suggestions during the entire project were invaluable.

I would like to thank the faculty members of the physics department at UNT, especially from the Ion Beam Modification and Analysis Laboratory (IBMAL). Direct and indirect support to this work provided by Dr. Bibhudutta Rout and Dr. Tilo Reinert are greatly appreciated. Special thanks are due to Dr. Floyd McDaniel for his valuable suggestions and mentoring throughout my graduate school time.

I would like to thank all the former and current students at IBMAL for all the support and encouragement, especially Dr. Jose Pacheco and Dr. Lucas Phinney.

Kurt Weihe, Gary Karnes and Paul Jones have been very helpful for their technical support. Thanks are due to Holly Decker for making necessary travel arrangements for conferences and Meloney Bowshier for providing help in purchasing items and countless other duties.

I must thank my wife, Pooja Singh for her support, patience and unconditional love. I also thank my sisters and my brother, as without their support all this would have been very difficult.

Finally, I dedicate this work to my parents for their love, for believing and always being there for me.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>CHAPTER 1 SPUTTERING OF Bi</td>
<td>1</td>
</tr>
<tr>
<td>1. Introduction and Motivation</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Sputtering Theory</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1. Elastic Collision Theory</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2. Linear Cascade Theory</td>
<td>4</td>
</tr>
<tr>
<td>1.2.3. Sigmund's Sputtering Yield Formula</td>
<td>6</td>
</tr>
<tr>
<td>1.2.4. Modified Matsunami's Empirical Formula</td>
<td>7</td>
</tr>
<tr>
<td>1.2.5. Computer Simulation</td>
<td>8</td>
</tr>
<tr>
<td>1.3. SRIM</td>
<td>9</td>
</tr>
<tr>
<td>1.3.1. Two Body Central Force Scattering</td>
<td>9</td>
</tr>
<tr>
<td>1.3.2. Magic Formula</td>
<td>12</td>
</tr>
<tr>
<td>1.3.3. Interatomic Potential</td>
<td>14</td>
</tr>
<tr>
<td>1.3.4. Nuclear Energy Loss and Angular Deflection</td>
<td>14</td>
</tr>
<tr>
<td>1.3.5. Simulation Environment</td>
<td>15</td>
</tr>
<tr>
<td>1.4. Experiment</td>
<td>16</td>
</tr>
<tr>
<td>1.4.1. Target Preparation</td>
<td>16</td>
</tr>
<tr>
<td>1.4.2. Incident Ion Beam</td>
<td>16</td>
</tr>
<tr>
<td>1.4.3. Sputtering Geometry</td>
<td>17</td>
</tr>
<tr>
<td>1.4.4. RBS</td>
<td>19</td>
</tr>
<tr>
<td>1.5. Results and Discussion</td>
<td>22</td>
</tr>
<tr>
<td>1.5.1. Ne on Bi</td>
<td>22</td>
</tr>
<tr>
<td>1.5.2. Ar on Bi</td>
<td>26</td>
</tr>
<tr>
<td>1.6. Summary</td>
<td>30</td>
</tr>
</tbody>
</table>
Table 1.1. Sputtering yield $Y$ (atoms/ion) as a function of energy for normally incident Ne$^+$ ions on a solid Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown. .......................................................... 25

Table 1.2. Sputtering yield $Y$ (atoms/ion) as a function of energy for normally incident Ar$^+$ ions on a solid Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown. .......................................................... 30

Table 2.1. Sputtering yield $Y$ (atoms/ion) for normally incident 50 keV Ar ions on Ga. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown. ... 44

Table 2.2. Experimental and simulated value of partial sputtering yield $Y_i$ (atoms/ion) for normally incident 25 keV Ar ions on Ga:Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown. .......................................................... 49

Table 2.3. Experimental and simulated value of partial sputtering yield $Y$ (atoms/ion) for normally incident 50 keV Ar ions on Ga:Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown. .......................................................... 52
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>The scattering event in a two-body collision in the center-of-mass coordinate system</td>
<td>11</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>The particle trajectories in the CM system</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Photograph of the interior of the sputtering chamber</td>
<td>17</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Schematic drawing of sputtering collector geometry</td>
<td>18</td>
</tr>
<tr>
<td>Figure 1.5</td>
<td>Layout of the accelerator facility in the Ion Beam Modification and Analysis Laboratory</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.6</td>
<td>RBS spectrum of Bi on Al collector foil using 2.0 MeV Si⁺</td>
<td>21</td>
</tr>
<tr>
<td>Figure 1.7</td>
<td>Plot of measured and fitted differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 50 keV Ne⁺ on polycrystalline Bi</td>
<td>22</td>
</tr>
<tr>
<td>Figure 1.8</td>
<td>Plot of measured and fitted differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV and 50 keV Ne⁺ on polycrystalline Bi</td>
<td>23</td>
</tr>
<tr>
<td>Figure 1.9</td>
<td>Plot of simulated [SRIM] and fitted differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV and 50 keV Ne on Bi</td>
<td>24</td>
</tr>
<tr>
<td>Figure 1.10</td>
<td>Plot of sputtering yield $Y$ (experiment) vs Ne⁺ ion energy $E$ compared to sputtering yield values predicted by Sigmund’s theory, the empirical formula of Matsunami et al., and values obtained from the SRIM code</td>
<td>27</td>
</tr>
<tr>
<td>Figure 1.11</td>
<td>Plot of measured and fitted differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV - 50 keV Ar⁺ on polycrystalline Bi</td>
<td>28</td>
</tr>
<tr>
<td>Figure 1.12</td>
<td>Plot of simulated [SRIM] and fitted differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV, 30 keV and 50 keV Ar on Bi</td>
<td>29</td>
</tr>
<tr>
<td>Figure 1.13</td>
<td>Plot of sputtering yield $Y$ (experiment) vs Ar⁺ ion energy $E$ compared to sputtering yield values predicted by Sigmund’s theory, the empirical formula of Matsunami et al., and values obtained from the SRIM code</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Photograph of the target holder in the UHV chamber with the liquid Ga:Bi binary alloy target</td>
<td>39</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Plot of measured and fitted differential sputtering yield of Ga as a function of polar angle for normally incident 50 keV Ar⁺ on liquid Ga</td>
<td>41</td>
</tr>
</tbody>
</table>
Figure C.3. Schematic of RBS setup and data acquisition electronics........................78

Figure C.4. RBS spectrum from Rh film using 3.0 MeV O$^{2+}$ beam .........................79

Figure C.5. Plot of apparent areal density of Rh on VC vs. bias voltage under varying experimental conditions..................................................................................................80

Figure C.6. Plot of apparent areal density of Pd on VC vs. bias voltage under varying experimental conditions.................................................................81
1.1. Introduction and Motivation

Sputtering, or the removal of material from a surface through the impact of energetic particles, was first observed by Grove in 1853 as the erosion of a cathode bombarded by energetic ions from a plasma. However, the subject reached maturity only after the theoretical paper by Sigmund on collisional sputtering in 1969. Sputtering has become an important tool in applications like thin film deposition, etching of surfaces in the semiconductor industry, and sputter ion sources. Indeed, surface analysis technique like Secondary Ion Mass Spectroscopy would not exist without sputtering. On the other hand, sputtering is one of the most critical problems in erosion of vessel walls by gas discharges, and contamination of the plasma in attempts to build a fusion reactor. A large number of experimental results on sputtering by energetic particle bombardment have been accumulated over several decades; however sputtering still remains a subject of significant interest.

The first chapter of this dissertation specifically deals with the sputtering of a single-element target. The sputtering of such targets has been investigated to a large extent. However, it still remains a subject of considerable interest. The investigation of the angular distribution of sputtered particles has been an effective means to obtain information about surface topography, target materials, and target structure [1]. Relatively fewer studies related to sputtering mechanisms have been done on semi-metallic targets like bismuth (Bi) as compared to other elements, and no experimental data have been reported so far for the angular distributions of atoms sputtered from Bi surfaces [2]. This element, which has specific properties like low binding energy and high sensitivity to electronic energy deposition, has recently received attention in ion beam applications and materials science [3, 4]. Bi nano-wires have been of great importance in nano-science and nano-technology to both theorists and experimentalists [5]. Recently, thin films of Bi-based compounds produced by thermal evaporation, sputtering and electrochemical deposition techniques have been topics of active
research [6, 7, 8]. Bi, along with other elements like Ga, Au, and Li, forms liquid metal alloys which are used in high beam brightness liquid metal ion sources (LMIS) for focused ion beam applications [9, 10, 11]. Despite the availability of theoretical and computational models, experimental data on the angular distribution of sputtered atoms are needed by modern technologies concerned with etching processes [12, 13] and high quality thin film production [14]. Recently Mammeri et al. [15] have reported the sputtering yield of Bi thin films deposited onto silicon substrates under the impact of 20 keV − 160 keV Ar\(^+\) ions, but not for bulk Bi.

In this study, sputtering yields of bulk Bi bombarded with 10 keV − 50 keV Ne\(^+\) and Ar\(^+\) ions are reported along with the angular sputtering distributions. A Monte-Carlo computer code, Stopping and Range of Ions in Matter (SRIM) [16], which employs the binary collision approximation to model collision cascades, has been used to obtain angular distributions of sputtered atoms and sputtering yields of Bi for 10 keV − 50 keV normally incident Ne and Ar ions. The sputtering yields of Bi from the current study are also compared to values obtained from Sigmund’s linear cascade theory [17] and the semi-empirical formula of Matsunami et al. [18]. In general, it is concluded that the process of Bi sputtering is quantitatively well-described by both models. The results from the present study enrich the existing sputtering yield database and also provide a reference point for experiments described later in this dissertation to measure the angular distribution of sputtered atoms from Bi:Ga liquid alloy that exhibits extreme surface segregation [19].

1.2. Sputtering Theory

According to Sigmund’s theory [17], three different collision cascade regimes can be distinguished, depending on the mass and energy of the incident ion:

1) Single knock-on regime.
2) Linear collision cascade regime.
3) Non-linear cascade regime (spikes).

In the single knock-on regime, the bombarding ions have enough energy to set only a few target atoms in motion, some of which may overcome the surface binding energy to get
sputtered. Mostly, this model pertains to the few to hundreds of eV region of projectile energy. However, in the case of light ions it may be extended to a few keV because the energy transfer is not adequate to sputter atoms at lower energies. The linear cascade regime falls in the keV energy region for most projectiles, where the incident ions have enough energy to set the target atom(s) in motion and to generate recoil cascades. However, due to the low density of recoil atoms, collisions between moving and stationary atoms prevail. The spike regime differs from the linear cascade regime in the sense that the former has a higher density of recoil atoms and hence most of the interacting atoms are in motion.

1.2.1. Elastic Collision Theory

The conservation laws of energy and momentum govern the energy transfer between atoms in an elastic collision. The maximum energy transferred elastically to an atom with zero initial energy when bombarded with an atom possessing energy $E$ is \[ T_m = \gamma E, \]

where

\[ \gamma = \frac{4M_1M_2}{(M_1 + M_2)^2} \]

and $M_1$ and $M_2$ are the atomic masses of the projectile and target, respectively.

The linear collision cascade regime applies in this study as keV ions are used to sputter the target. According to Lindhard et al. [21] the screening of the Coulomb interaction between atoms is important in this regime, and the scattering cross section differential in energy is approximated by the expression

\[ d\sigma(E,T) \approx C_mE^{-m}T^{-1-m}dT \quad \text{for} \quad 0 \leq T \leq T_m \]

where

\[ C_m = \frac{\pi}{2}\lambda_m a^2 \left( \frac{M_1}{M_2} \right)^m \left( \frac{2Z_1Z_2e^2}{a} \right)^{2m} \]
and

$E$, $M_1$ and $M_2$ are as described in equations (1) and (2);

$T$ is the energy transferred to the target atom;

$a$ is the Thomas-Fermi screening radius;

$Z_1$ and $Z_2$ are the atomic numbers of incident and target atoms, respectively; and

$\lambda_m$ is a dimensionless function of the parameter $m$ which varies gradually from $m \approx 0$ at very low energies to $m = 1$ at high energies.

The average energy spent in elastic collisions by the beam particles traversing path length $x$ in the target with atomic concentration $N$ is given by

\begin{equation}
\Delta E =Nx \int d\sigma(E, T) T \equiv N x S_n(E)
\end{equation}

where $S_n(E)$ is called the nuclear stopping cross section and is given by

\begin{equation}
S_n(E) = 84.78 \frac{Z_1 Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}} \left( \frac{M_1}{M_1 + M_2} \right) s_n(\epsilon),
\end{equation}

where the reduced energy $\epsilon$ is

\[ \epsilon = \frac{0.03255}{Z_1 Z_2 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2}} \left( \frac{M_2}{M_1 + M_2} \right) E, \]

and $s_n(\epsilon)$ is the universal function tabulated in Table I in [17] and

\[ s_n(\epsilon) \propto \frac{\gamma^{1-m}}{1-m} E^{1-2m}. \]

The expressions (3), (4) and (6) are based on the Thomas-Fermi model of atomic interaction. It is observed that $S_n(E)$ rises in proportion to $E$ at low energies ($m \approx 0$), approaches a plateau at intermediate energies ($m \approx 1/2$) and falls off at higher energies ($1/2 < m \leq 1$) [21].

1.2.2. Linear Cascade Theory

Let $n(E, E_0)$ be the average number of atoms set in motion with energy greater than some threshold $E_0$, in a cascade started by an ion with energy $E$ greater than $E_0$ [22]. One
can write

\[ n(E, E_0) \sim \Gamma_m \frac{E}{E_0} \]

where \( \Gamma_m \) is a function involving the gamma function and has a value of 0.608 for \( m = 0 \), which pertains to this study. Some part of the energy of the incident ion is also used for the excitations of electrons in target atoms and hence the amount of energy available for the collision cascade decreases to

\[ \nu(E) = E - \eta(E) \]

where \( \eta(E) \) is the average amount of energy lost to electronic excitation. Also, \( \nu(E) \) depends on ionic mass [23] as electronic stopping depends on velocity rather than energy [24]. After all tools are set, one can obtain the recoil density \( F(E, E_0) \) in a given energy interval \((E_0, \, dE_0)\) from Eqns. (7) and (8) and calculate the depth profile of the deposited energy density as [25, 26]

\[ F_D(E, \theta, x) = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz F_D(E, \vec{\Omega}, \vec{r}), \]

where the \( x \) axis is normal to the target surface and to which beam direction \( \vec{\Omega} \) makes an angle \( \theta \). The density of the deposited energy, \( F_D(E, \vec{\Omega}, \vec{r}) \), originates from the conservation of energy expression

\[ \int d^3r F_D(E, \vec{\Omega}, \vec{r}) = \nu(E). \]

The outward current of target atoms through the surface plane \( x = 0 \) is found similarly to equation (9) and is given by

\[ J(E_0, \vec{\Omega}_0) dE_0 d^2\Omega_0 = \psi F_D(E, \theta, 0) \frac{\Gamma_m dE_0}{E_0 \left| \frac{dE_0}{dx} \right|} \cos \theta_0 \frac{d^2\Omega_0}{4\pi} \]

where \( \psi \) is the number of projectiles per unit time of initial energy \( E \), and \( \theta_0 \) is the angle between the surface normal and \( \vec{\Omega}_0 \).
1.2.3. Sigmund’s Sputtering Yield Formula

If \( P(E_0, \theta_0) \) is the probability for an atom at the surface moving with \( E_0 \) at \( \theta_0 \) to escape from the surface, then the sputtering yield \( Y \) can be calculated by integrating equation (10) over \( E_0 \) and \( \theta_0 \), or

\[
Y = \Lambda F_D(E, \theta, 0)
\]

with

\[
\Lambda = \frac{\Gamma_m}{2} \int \frac{dE_0}{E_0} |\frac{dE_0}{dx}| \int d(\cos \theta_0)| \cos \theta_0| P(E_0, \theta_0).
\]

After incorporating the angular dependence of the particle escape probability, the refraction effect of a particle passing through a planar potential step and the term for the nuclear stopping cross section, Sigmund’s theory predicts a cosine-like distribution:

\[
\frac{dY}{d\Omega} \sim \cos^n \theta \quad \text{where} \quad n \approx 1.
\]

\( dY/d\Omega \) is the differential angular sputtering yield in a solid angle \( d\Omega \) and \( \theta \) is the polar angle of the emitted particle’s trajectory. The analytic solution incorporating electronic stopping, the cross section for elastic scattering, surface binding forces, zero and higher order moments of the particle distribution function and the depth of origin of sputtered atoms to determine terms in Eq. (11) yields [17]

\[
\Lambda = \frac{3}{4\pi^2} \frac{1}{NC_0 U_b},
\]

where \( N \) is the density of the target atoms, \( U_b \) is the surface binding energy of the target atom and

\[
C_0 = \frac{1}{2} \pi \lambda_0 a^2, \quad \lambda_0 = 24, \quad a = 0.219 \ \text{Å}.
\]

The transformation of Eq. (12) to Eq. (13) is described in detail in [17]. The energy dependence of the sputtering yield is determined by the stopping power in the linear collision
cascade regime. Hence, for normally incident projectiles the sputtering yield can be written as

\[ Y(E) = \Lambda \alpha N S_n(E). \]

where \( S_n(E) \) is the elastic stopping power of the ion \([\text{given by Eq. (6)}]\) and \( \alpha \) is a factor that depends only on \( m \) and \( M_2/M_1 \). An approximate value of the factor \( \alpha \) for a given ion-target combination in the elastic collision regime can be found from Fig. 13 in [17]. Combining Eqs. (11) and (12), one can obtain the expression for the sputtering yield at normal incidence as

\[ Y(E) = \frac{0.042\alpha S_n(E)}{U_b}. \]

1.2.4. Modified Matsunami’s Empirical Formula

Based on sputtering yield data available in early 1983, an empirical formula which could predict the energy dependence of the sputtering yield for any ion-target combination was proposed by Matsunami and his coworkers [18]. Yamamura and Tawara have used the large amount of experimental sputtering data published during 1983-1994 and revised the empirical formula in [18] to give a new empirical formula [27]. This section briefly summarizes the empirical formula used in this work to calculate the energy dependence of the sputtering yield for normally incident keV ions.

The empirical formula uses the following analytical expression based on the Thomas-Fermi potential for the reduced nuclear stopping power:

\[ S_{n,TF}(\epsilon) = \frac{3.441\sqrt{\epsilon}\ln(\epsilon + 2.718)}{1 + 6.355\sqrt{\epsilon} + \epsilon(6.882\sqrt{\epsilon} - 1.708)}. \]

Here, the reduced energy is the same as the one expressed in Section 1.2.1. The empirical formula uses the Lindhard electronic stopping coefficient \( k_e [24] \):

\[ k_e = 0.079\frac{(M_1 + M_2)^{3/2}}{M_1^{3/2}M_2^{1/2}} \frac{Z_1^{2/3}Z_2^{1/2}}{(Z_1^{2/3} + Z_2^{2/3})^{3/4}}. \]

A normally incident light ion \([\text{e.g., } H^+ \text{ or } D^+]\) is unable to produce a collision cascade near the surface. Instead, the ions are reflected from beneath the surface layer, hitting the surface atoms and sputtering those recoil atoms whose kinetic energies are able to overcome
the surface binding energy. The empirical formula uses the parameter \( \Gamma \) to describe the contribution to the sputtering yield from such a process:

\[
(18) \quad \Gamma = \frac{W(Z_2)}{1 + (M_1/7)^3}.
\]

The best-fit value of the dimensionless parameter \( W(Z_2) \) is listed in Table. I in [27].

The empirical formula is given as

\[
(19) \quad Y(E) = 0.042Q(Z_2)\alpha^*(M_2/M_1)\frac{S_n(E)}{U_b} \times \left[ 1 - \frac{\gamma k_e e^{0.3}}{\sqrt{E/E_{th}}} \right]^s
\]

where the best-fit value of the dimensionless parameter \( Q(Z_2) \) is listed in Table. I in [27], \( \gamma \) is as described in Eq. (2), and the nuclear stopping cross section \( S_n(E) \) is the same as in Eq. (6). The best-fit value of \( \alpha^* \) is described by the expression

\[
(20) \quad \alpha^* = 0.249(M_2/M_1)^{0.56} + 0.0035(M_2/M_1)^{1.5}, \quad M_1 \leq M_2,
\]

and a best-fit functional relation is used for the sputtering threshold energy \( E_{th} \):

\[
(21) \quad E_{th} = \frac{1 + 5.7(M_1/M_2)}{\gamma} U_b, \quad M_1 \leq M_2.
\]

Sigmund’s formula [Eq. (15)] neglects the energy loss of the sputtered atoms between the point of origin and the surface. The empirical formula incorporates the \( Z_2 \) dependence of \( \alpha \) through \( Q(Z_2) \); i.e., it takes into account the recoiling particle energy loss in traversing the target material. The value of the sputtering yield for any ion-target combination evaluated using Eq. (19) is accurate to within \( \pm 20\% \) near the maximum of the sputtering yield. Deviations are found to be \( \geq 20\% \) for lower (\(< 1 \text{ keV}\)) and higher energies (\(> 100 \text{ keV}\)) due to scarcity of experimental data.

1.2.5. Computer Simulation

A series of atomic collisions between incident particles and target atoms, leading to collisions between target atoms themselves, lies behind the sputtering process. Computer simulations make it fairly simple to understand these collision cascades. Two major approaches with computer simulations are the binary collision approximation (BCA) and
molecular dynamics (MD) calculations. MD simulates the time evolution of the multiple interactions of each atom with all the atoms in some surrounding, and BCA describes the process of sputtering as a sequence of independent binary collisions between atoms. In BCA simulations it is assumed that the collisions between atoms can be approximated by elastic binary collisions described by an interaction potential. Also, it is assumed that energy transfer to electrons can be handled separately as an inelastic energy loss. Results from BCA simulations have shown good agreement with experimental results [28, 29]. The Transport of Ions in Matter (TRIM) code included in the Stopping and Range of Ions in Matter (SRIM), based on BCA, is widely used for sputtering simulations [16]. Besides sputtering yield calculations, it also helps in the determination of angular distributions of sputtered atoms.

1.3. SRIM

The Stopping and Range of Ions in Matter (SRIM) is a Monte Carlo computer program that calculates the interactions of energetic ion with solid targets. The program uses several physical approximations to obtain high computational efficiency, while still maintaining accuracy. The two most important approximations that the code uses are (1) an analytical formula for determining atom-atom collision outcomes and (2) the concept of free flight path between collisions, so that only significant collisions are evaluated. In the latter approximation the incident ion typically skips over several monolayers in the target before encountering its first collision. By doing so, the simulation time can be reduced by a significant amount. However, sputtering is a surface phenomenon; hence monolayer collision steps were preferred over the free flight path approximation in this entire study to better extract the collision cascades which play a vital role in the angular distributions of sputtered atoms. The following section briefly discusses the first approximation that the SRIM code uses.

1.3.1. Two Body Central Force Scattering

We will be using the center-of-mass coordinate system (CM) since the relative motion of the particles can be reduced to that of a single particle moving in a central potential (called
the interatomic potential discussed later) centered at the origin of the CM coordinates. When one wants to find the cross-section for the energy transferred in a scattering event, evaluating the details of the scattering trajectories and hence evaluating the probability of scatter into each scattering angle is inevitable. To simplify this problem, one can assume that the force between two particles acts only along the line joining them, and there are no transverse forces. In the CM system the paths of the two particles are symmetric; hence, the net momentum of the particles is always zero. Fig. 1.1 shows the scattering variables in a two-body collision. 

\[ M_1 \text{ and } M_2 \] are the masses of the projectile and the target atom, respectively. The initial velocities of the projectile and the target atom in the laboratory coordinate system are \( \vec{v}_0 \) and zero, respectively. The projectile has impact parameter \( p \) with the target particle, and \( r \) is the interatomic separation.

We can use Lagrangian mechanics in polar coordinates to derive the scattering angle. Let \( \Theta \) and \( r \) be the polar and radial coordinates, respectively. Thus, conservation of energy for such a system in CM frame gives

\[
(22) \quad E_c = \frac{1}{2} M_c (\dot{r}^2 + r^2 \dot{\Theta}^2) + V(r),
\]

where

\( E_c = \frac{1}{2} M_c v_0^2 \) is the CM energy,

\( M_c = \frac{M_1 M_2}{M_1 + M_2} \) is the reduced mass in the CM coordinates,

\( \dot{r} \) is the time derivative of the radial coordinate, \( r \),

\( \dot{\Theta} \) is the time derivative of the polar coordinate, \( \Theta \),

and \( V(r) \) is the central force field potential energy.

Conservation of angular momentum for the system in CM coordinates gives

\[
(23) \quad J_c = M_c r^2 \dot{\Theta},
\]

where \( J_c \), the constant angular momentum with respect to the origin, can be related to
Figure 1.1. The scattering event in a two-body collision in the center-of-mass coordinate system. The coordinate system moves with velocity $\vec{v}_c$ relative to laboratory coordinates. $\Theta$ and $\Phi$ are the scattering angle of the projectile and the recoil angle of the target mass, respectively.

Impact parameter $p$ by

$$J_c = M_c v_0 p.$$  \hfill (24)

Eqs. (22) – (24) can be solved to get

$$\dot{r} = v_0 \left[1 - \frac{V(r)}{E_c} - \left(\frac{p}{r}\right)^2\right]^{1/2}. \hfill (25)$$

Also from Eqs. (23) and (24) it is clear that

$$\dot{\Theta} = \frac{v_0 p}{r^2}. \hfill (26)$$
Hence, combining the equations for $\dot{r}$ and $\dot{\Theta}$, we get

$$d\Theta/dr = \frac{\dot{\Theta}}{\dot{r}} = \frac{p}{r^2 \left[ 1 - \frac{V(r)}{E_c} - \left( \frac{p}{r} \right)^2 \right]^{1/2}}. \tag{27}$$

Eq. (27) can be integrated over the entire collision path to get the final angle of scatter:

$$\Theta = \pi - 2 \int_{r_0}^{\infty} \frac{pdr}{r^2 \left[ 1 - \frac{V(r)}{E_c} - \left( \frac{p}{r} \right)^2 \right]^{1/2}} \tag{28}$$

with the condition for the minimum distance of approach given by

$$\left[ 1 - \frac{V(r)}{E_c} - \left( \frac{p}{r} \right)^2 \right] = 0. \tag{29}$$

Thus the distance of closest approach is

$$r_0 = \frac{p}{\sqrt{1 - \frac{V(r)}{E_c}}}. \tag{30}$$

From Eq. (28) it is clear that the final scattering angle of both the ion and the recoil, $\Theta$, can be determined from $E_c$, $V(r)$, and $p$. A problem arises when a computer has to evaluate the scattering integral for all possible collisions, which could be a time-consuming process. SRIM employs an analytical technique to solve the atom-atom scattering, called the “Magic Formula” and discussed in the next section. The main advantage of using this technique is that the computing time is reduced by $\approx 50$ times as compared to other techniques.

1.3.2. Magic Formula

The technique for determining the atom-atom collision called the “Magic Formula” was developed by Biersack and Haggmark [30]. The formalism incorporated into their computer program is applicable to a large variety of ion-target combinations, and it provides useful information on the range of an ion in a target and details about the sputtering mechanism. Fig. 1.2 illustrates the scattering through an angle $\Theta$ of an incident particle of mass $M_1$ and kinetic energy $E$, by an initially stationary particle of mass $M_2$ for a repulsive interaction potential. The “scattering triangle” comprises the known or easily accessible quantities radii of curvature $\rho_1$ and $\rho_2$, impact parameter $p$, small correction terms $\delta_1$ and $\delta_2$, and distance of closest approach $r_0$. 

12
Figure 1.2. The particle trajectories in the CM system. Also shown is the “scattering triangle”, constructed from radii of curvature $\rho_1$ and $\rho_2$, impact parameter $p$, correction terms $\delta_1$ and $\delta_2$ and distance of closest approach $r_0$.

From the scattering triangle it immediately follows that

\[
\cos \left( \frac{\Theta}{2} \right) = \frac{\rho + p + \delta}{\rho + r_0}
\]

with

\[
\begin{align*}
\rho &= \rho_1 + \rho_2 \\
\delta &= \delta_1 + \delta_2
\end{align*}
\]

The radius of curvature in the CM system is given as [30]

\[
\rho = \frac{2[E_c - V(r_0)]}{-V'(r_0)}
\]

where $V'(r_0)$ is the spatial derivative of the potential evaluated at $r_0$. 

13
Eq. (31) is written in terms of a universal screening length $a$ and fitting parameter $\Delta$ as

\begin{equation}
\cos \left( \frac{\Theta}{2} \right) = \frac{B + R_C + \Delta}{R_0 + R_C} \quad \text{(MAGIC FORMULA)},
\end{equation}

where

\begin{equation}
B = \frac{p}{a}, R_0 = \frac{r_0}{a}, R_C = \frac{\rho}{a}, \Delta = \frac{\delta}{a} \quad \text{and} \quad a = \frac{0.8853a_0}{Z_1^{2/3} + Z_2^{2/3}}.
\end{equation}

Details of fitting the magic parameter $\Delta$ are described in detail in [30]. The above formula allows fast determination of the scattering angles of both the ion and the recoil with high precision.

1.3.3. Interatomic Potential

The term $V(r)$ in Eq. (22) is the potential energy associated with the central force field which is the combined field of the two particles, and is called the interatomic potential. Based on a study by Wilson et al. [31], SRIM uses the Molière approximation [32] to the Thomas-Fermi potential for nuclear scattering and energy loss in its ion transport simulation as it is a more suitable universal potential as compared to the Sommerfeld [33] or Bohr potentials [20]. This potential is expressed as

\begin{equation}
V(R) = \frac{Z_1 Z_2 e^2}{a R} \Phi(R),
\end{equation}

where $R = r/a$ is the reduced interatomic separation and $\Phi(R)$ is the Molière screening function, given as

\begin{equation}
\Phi(R) = 0.35 \ e^{-0.3R} + 0.55 \ e^{-1.2R} + 0.1 \ e^{-6R}.
\end{equation}

1.3.4. Nuclear Energy Loss and Angular Deflection

The energy transfer (nuclear energy loss), $T$, in an elastic collision is directly proportional to $\sin^2(\Theta/2)$ and is given by

\begin{equation}
T = \frac{4M_1 M_2}{(M_1 + M_2)^2} E \sin^2 \left( \frac{\Theta}{2} \right).
\end{equation}
The scattering angle in the laboratory frame of reference is given by the following expression:

\begin{equation}
\vartheta = \arctan\left(\frac{\sin \Theta}{\cos \Theta + (M_1/M_2)}\right).
\end{equation}

After the collision, the azimuthal scattering angle \( \phi \) for both the projectile and the target atom is randomly selected using the relation

\begin{equation}
\phi = 2\pi R_n,
\end{equation}

where \( R_n \) is a random number uniformly distributed between 0 and 1. SRIM follows the particles in the actual calculation with reference to the axis normal to the target surface. The angle, \( \alpha \), with respect to the axis normal to the target surface is determined after each collision, and the cosine of this angle after the \( i \)th collision is given as

\begin{equation}
\cos \alpha_i = \cos \alpha_{i-1} \cos \vartheta_i + \sin \alpha_{i-1} \sin \vartheta_i \cos \phi_i.
\end{equation}

1.3.5. Simulation Environment

Computer simulation were performed with the SRIM code. To adequately treat the near-surface interactions important to sputtering, monolayer collision steps were selected instead of the free flight path approximation in the simulation. To ensure that there were no transmitted atoms contributing to the sputtering yield, 400 nm and 220 nm thick Bi targets were chosen after several trial simulations for normally incident Ne and Ar ion bombardment, respectively. The heat of sublimation of Bi, equal to 2.17 eV, was used in calculations as the value of the surface binding energy. A typical simulation consisted of approximately 70,000 and 180,000 sputtered particles for Ne and Ar ion bombardment, respectively, to analyze the angular distribution. During the simulation, the polar and the azimuthal angles of the sputtered atoms’ traveling directions were documented as well. The ejection angles were collected into multiple polar angle bins with a size of 5°, and the counts were normalized by dividing by the number of projectiles to obtain the sputtering yield differential in angle.
1.4. Experiment

1.4.1. Target Preparation

High purity (99.9999%) bismuth shot from Cominco Electronic Materials was flattened onto a tantalum disc using a mechanical press to produce a $\sim 60 \text{ mm}^2$ circular and $\sim 1 \text{ mm}$ thick Bi sample. To remove any accumulated oxide layer, the target was etched with $\text{H}_2\text{SO}_4$ diluted with deionized water. After a two min ultrasonic bath in diluted $\text{H}_2\text{SO}_4$, the target was rinsed in deionized water and methanol, and warm air dried before being loaded into the ultra high vacuum (UHV) target chamber.

1.4.2. Incident Ion Beam

A 200 kV Cockcroft Walton accelerator with a radio-frequency (RF) type ion source was used to produce 10 keV – 50 keV Ne$^+$ and Ar$^+$ ion beams used for sputtering. The RF ion source can produce an ion beam composed of $\approx 90\%$ singly ionized ions. Source gas entering the Pyrex bottle through a leak valve is ionized by an RF field applied to the two excitor rings, followed by the extraction of positive ions through the exit canal by applying a potential difference across the bottle. The ions leaving the canal are focused by applying 0 – 10 kV negative (with respect to ion source base) voltage on the gap lens. After leaving the gap lens, the ion beam enters the accelerating tube, to which high voltage is applied by means of a regulated 0 – 50 kV power supply. After the acceleration stage, the ion beam passes through an electrostatic quadrupole lens, horizontal and vertical slits, a 45-degree analyzing magnet, and another set of horizontal and vertical slits [34]. Fig 1.3 shows a photograph of the interior of the UHV chamber. Before entering the UHV chamber, the beam of typically $\sim 100 \text{ nA}$ passes through a custom designed electrostatic quadrupole triplet ion beam lens [35] which focuses the beam to a diameter of $\sim 50 \mu\text{m}$ on the target. The beam current is measured using two Faraday cups, each positioned after the sets of horizontal and vertical slits. Both the cups have biased $-100 \text{ V}$ rings to suppress any secondary electrons.
1.4.3. Sputtering Geometry

Sputtering geometry plays a vital role in measuring the sputtering yields of elements and angular distributions of the sputtered atoms. Misalignments in the sputtering geometry are ineluctable for an experimentalist; however compensation for these misalignments is essential. The possible offsets in the sputtering geometry are described in detail in Appendix A. A schematic of the sputtering geometry is shown in Fig 1.4. The target was positively biased with respect to the collector to suppress any secondary electrons leaving the target. A target bias of +36 V for the 50 keV Ar$^+$ beam was chosen after a series of measurements to suppress any secondary electrons and tertiary electrons reaching the collector foil holder. This procedure was repeated for the different incident ions for different energies. The current
Figure 1.4. Schematic drawing of sputtering collector geometry. The bias on the target is to suppress secondary and tertiary electrons. The foil radius is 23 mm.

from the target was integrated to measure beam fluence. To collect the sputtered material, 99.995\% pure aluminum foil was cut into 9 mm × 71 mm strips, which were mounted in cylindrical holders that could be placed in front of the target. A hole was cut in the center of each strip to allow passage of the ion beam. A cross-sectional view of a foil strip in position for collection is shown schematically in Fig. 1.4. To avoid the collection of any contamination on the Bi target, a spot on the target was initially sputtered with an integrated charge of ~20 µC, at which point a fresh collector foil was placed in position and the target was sputtered with an integrated charge of ~1000 µC. This procedure was followed for every sputtering collection measurement.
Figure 1.5. Layout of the accelerator facility in the Ion Beam Modification and Analysis Laboratory.
After sputtering, the collector foils were removed from the UHV chamber and mounted on a target holder in an analysis chamber attached to the IBMAL’s 3 MV National Electrostatics Corporation Tandem Pelletron (9SDH-2) accelerator [36, 37]. Fig. 1.5 shows a layout of the accelerator facility in the IBMAL’s main laboratory. A 2.0 MeV Si$^+$ beam was then used to perform Rutherford backscattering spectrometry (RBS) to measure the areal density of the Bi along the length of the Al collector foil. A projectile species more massive than Al was desired to obtain a spectrum of backscattered ions from sputtered material only, without any contribution from the Al, and Si was a convenient choice. For these measurements, a $\sim$2 mm diameter, $\sim$5 nA beam was used, and an integrated charge of $\sim$1 $\mu$C $-$ 2 $\mu$C was accumulated at each position. Many factors affect the accuracy of current integration measurements when fast ions impinge upon a solid target [38]. The experimental set up for RBS and the methods for accurate current integration used for the collector foil analysis are described in detail in Appendix C.

Fig. 1.6 shows a representative Si backscattering spectrum of sputtered Bi on an Al collector foil. The breadth of the backscattered peak is attributed primarily to the pulse height defect for the heavy Si ions in the solid state detector [39]. The asymmetrical response of the solid state surface barrier detector observed in Fig. 1.6 is typical for MeV heavy ions [40]. The detector had an active area of $\sim$44 mm$^2$ and was placed $\sim$8 cm from the manipulator holding the collector foil, at a scattering angle of $\sim$155°. The differential sputtering yield $dY/d\Omega$ was obtained by converting the measured Bi areal densities on the collector foil; this conversion included a small correction for misalignment in the sputtering geometry. The resulting differential angular sputtering yield data were fitted with the function

$$\frac{dY}{d\Omega} = A \cos^B \theta$$  \hspace{1cm} (41)

where $A$ (atoms/steradian-ion) and $B$ are the fit parameters. This fitted function, when integrated over the $2\pi$-steradians of the hemisphere in front of the target surface, gives the total sputtering yield,

$$Y = \int_0^{2\pi} d\phi \int_0^{\pi/2} A \cos^B \theta \sin \theta d\theta = \frac{2\pi A}{B + 1}.$$  \hspace{1cm} (42)
Figure 1.6. RBS spectrum of Bi on Al collector foil using 2.0 MeV Si$^+$. The spectrum shown is for $\sim$15.7° from target normal for 50 keV Ar$^+$ on Bi for a sputtering beam dose of $\sim$6.3 × 10$^{15}$ ions.

The error analysis included the statistical uncertainty in the areal densities from the RBS measurements, uncertainties in current integration and RBS detector solid angle, and uncertainty from the nonlinear curve fit. Note that the calculated yield assumes a collection efficiency of unity, i.e., that all the sputtered Bi atoms incident on the collector foil surface stuck. The sticking probability for sputtered Bi on Al collector foil was not measured. However, similar measurements for Ag and Au on oxidized Al have been performed and it was concluded that under UHV conditions the sticking probabilities were 0.8 ± 0.2 and 0.92 ± 0.08 for Ag and Au, respectively [41].
1.5. Results and Discussion

1.5.1. Ne on Bi

Fig. 1.7 shows a plot of differential sputtering yield vs. polar angle in the sputtering geometry for 50 keV Ne$^+$ on solid Bi. The angular distribution obtained from the collector foil analysis is not corrected here for the offsets in the sputtering geometry discussed in Appendix A in detail. In Fig. 1.7 the areal density of Bi atoms on the collector foil when measured using the surface energy approximation ranged from $\sim 1.3 \times 10^{13}$ atoms/cm$^2$ to $2.0 \times 10^{15}$ atoms/cm$^2$. The Si energy loss in the thickest spot on the film is negligible ($< 1.5$
keV for 2.0 MeV Si beam) [42], hence the use of surface energy approximation to determine the areal density of sputtered material on the foil is justified [Appendix B].

\[ \text{Figure 1.8.} \text{ Plot of measured and fitted [using a modification of Eq. (41) as described in Appendix A] differential sputtering yield (atoms/steradian-ion) vs. polar angle } \theta \text{ (degrees) for 10 keV and 50 keV Ne}^{+} \text{ on polycrystalline Bi. Relative uncertainties for measured values were due to counting statistics in the RBS analysis.} \]

Sigmund’s linear cascade theory predicts a cosine distribution of sputtered atoms, assuming an isotropic flux of low energetic recoils beneath the solid surface. However, in the present study we have observed an over-cosine distribution of sputtered Bi atoms, both experimentally and by computer simulation. In this study we have used 10 keV and 50 keV Ne\(^{+}\) ions to probe the dependence of the angular distribution and sputtering yield on bombarding ion energy. Fig. 1.8 shows the measured and fitted [using Eq. (41)] differential sputtering yields for normally incident Ne\(^{+}\) ions on Bi. Relative uncertainties (±1σ) for
Figure 1.9. Plot of simulated [SRIM] and fitted [using Eq. (41)] differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV and 50 keV Ne on Bi. Approximately, 80,000 and 73,000 sputtered atoms were analyzed for 10 keV and 50 keV Ne on Bi, respectively.

The measured values were due to counting statistics in the RBS analysis, and ranged from $\sim 1.3\%$ near $0^\circ$ to $\sim 8.5\%$ near $-90^\circ$ for 10 keV Ne and $\sim 1.0\%$ near $0^\circ$ to $\sim 6.0\%$ near $90^\circ$ for 50 keV Ne. The values for the fitting parameter $A$ (atoms/ion-steradian) and $B$ along with their relative uncertainties are provided in Table 1.1. The over-cosine shape ($B > 1$) of the angular distribution of the sputtered atoms is typical of that observed for other polycrystalline metals, both experimentally and in computer simulations [43, 27, 44, 45]. Additionally, the sharpness of the angular distribution was found to be greater for 50 keV projectiles ($B = 2.4$) than for 10 keV projectiles ($B = 1.9$) and hence implies that the degree to which the distribution is over-cosine increases with increasing ion energy for normally incident Ne$^+$ in the measured energy regime. Sigmund and co-workers have observed that recoils originating from deeper
Ion−Energy Pair  Methodology  $A$  $B$  $Y$

<table>
<thead>
<tr>
<th>Ion−Energy Pair</th>
<th>Methodology</th>
<th>$A$ (atoms/steradian-ion)</th>
<th>$B$ (atoms/ion)</th>
<th>$Y$ (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 keV Ne</td>
<td>Expt</td>
<td>0.54 ± 0.04</td>
<td>1.98 ± 0.11</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>10 keV Ne</td>
<td>Simulation</td>
<td>1.60 ± 0.01</td>
<td>2.78 ± 0.02</td>
<td>2.66 ± 0.02</td>
</tr>
<tr>
<td>50 keV Ne</td>
<td>Expt</td>
<td>1.5 ± 0.1</td>
<td>2.4 ± 0.1</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>50 keV Ne</td>
<td>Simulation</td>
<td>1.44 ± 0.01</td>
<td>2.68 ± 0.02</td>
<td>2.45 ± 0.02</td>
</tr>
</tbody>
</table>

Table 1.1. Sputtering yield $Y$ (atoms/ion) as a function of energy for normally incident Ne$^+$ ions on a solid Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown.

layers will be preferentially ejected into a narrow cone around the surface normal [46]. This suggests that the contribution to the overall sputtering yield by recoils produced deeper in the target is higher for normally incident 50 keV Ne$^+$ on Bi than for normally incident 10 keV Ne$^+$. Fig. 1.9 shows the simulated [using SRIM] and fitted differential sputtering yields for normally incident Ne on Bi. It is clear from the figure that the simulated angular distributions of sputtered Bi atoms are also over-cosine in nature; however, in contrast to the experimental results, the shape of the angular distribution did not change significantly with ion energy in these simulations. Overall, there is good agreement between the shapes of the experimental and simulated angular distributions of sputtered Bi atoms for normally incident 50 keV Ne, and somewhat less so for 10 keV Ne, as can be observed in Figs. 1.8 and 1.9 and Table. 1.1.

Fig. 1.10 shows a plot of experimental sputtering yield $Y$ vs. normally incident Ne$^+$ ion energy $E$. Sputtering yields for keV Ne projectiles normally incident on Bi obtained from different models are also shown in the figure. The experimental yield $Y$ was observed to increase by a factor of $\sim 2.5$ when the Ne$^+$ energy increased from 10 keV to 50 keV, whereas the yields obtained from Sigmund’s theory [17] and the semi-empirical formula of Matsunami
et al. [18] increase by ≤ 20% for this same change in projectile energy, and the yield obtained from the SRIM simulation actually decreased slightly. The value for the surface binding energy for Bi used in these three models was 2.17 eV. Kudriavtsev and his co-workers have proposed a model based on an electronegativity concept to calculate the surface binding energy of particles sputtered from a solid surface by ion bombardment [47]. The value of the surface binding energy of Bi using this model is 3.71 eV, and the yields predicted by [17] and [18] using this surface binding energy are also shown in Fig. 1.10. The sputtering yield measured for normally incident 50 keV Ne$^+$ on Bi was close to the value obtained from SRIM, and was lower by at least a factor of two than the values predicted by the other models. The measured sputtering yield obtained for 10 keV Ne$^+$ was low compared to the yields obtained from all the models including SRIM. Note that the experimental yields are the average yields over the projectile fluence range $\sim 3.1 \times 10^{18} \text{atoms/cm}^2 - 3.1 \times 10^{20} \text{atoms/cm}^2$, whereas the simulated yields and yields from Sigmund’s theory are for the zero-fluence limit.

1.5.2. Ar on Bi

In this study we have also used 10 keV – 50 keV Ar$^+$ ions to sputter Bi, and have measured the resulting angular distributions and sputtering yields. Fig. 1.11 shows the measured and fitted differential sputtering yields as a function of polar angle $\theta$ for normally incident Ar$^+$ ions on Bi. For 50 keV Ar$^+$ on Bi, the areal density of Bi atoms on the collector foil when measured using the surface energy approximation ranged from $\sim 2.5 \times 10^{13} \text{ atoms/cm}^2$ to $6.1 \times 10^{15} \text{ atoms/cm}^2$. The angular distributions of sputtered Bi atoms were found to be over-cosine; however, the shape of the distribution was observed not to depend significantly on incident Ar energy over the energy range studied. The values for the fitting parameters $A$ (atoms/ion-steradian) and $B$ for 10 keV – 50 keV normally incident Ar$^+$ ions along with their uncertainties are provided in Table 1.2. Simulated and fitted differential sputtering yields plotted as a function of polar angle $\theta$ for normally incident 10 keV, 30 keV and 50 keV Ar on Bi are shown in Fig. 1.12. Generally good agreement between the shapes of the measured and simulated angular distributions is observed from Figs. 1.11 and 1.12, although the simulated distributions are slightly sharper than the measured distributions.
Plot of sputtering yield $Y$ (experiment) vs Ne$^+$ ion energy $E$ compared to sputtering yield values predicted by Sigmund’s theory, the empirical formula of Matsunami et al., and values obtained from the SRIM code. Sputtering yield values obtained by using the Bi surface binding energy predicted by Kudriavtsev et al. with Sigmund’s theory and the empirical formula of Matsunami et al. are also shown.

Fig. 1.13 shows a plot of experimental sputtering yield $Y$ vs. normally incident Ar$^+$ ion energy $E$. Also shown are plots of $Y$ vs. $E$ for Ar on Bi obtained using the same models as for Ne in the previous section. The experimental yield $Y$ was observed to increase with increasing ion energy, by a factor of $\sim 2$ as the Ar$^+$ energy increased from 10 keV to 50 keV, with most of the increase occurring between 10 keV and 40 keV. In comparison, the yields predicted by Sigmund’s theory and the semi-empirical formula of Matsunami et al. increase by $\sim 30\%$ for this same change in projectile energy, and the yield obtained from the
Figure 1.11. Plot of measured and fitted [using a modification of Eq.(41) as described in Appendix A] differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV − 50 keV Ar⁺ on polycrystalline Bi. Random uncertainties (±1σ) in the measured values are smaller than the size of the plotted symbols.

SRIM simulation is approximately constant. The measured sputtering yield for 10 keV Ar is close to the values predicted by Sigmund’s theory and the Matsunami formula if one uses the value of 3.71 eV for the surface binding energy of Bi instead of 2.17 eV, and is lower than the values obtained from the various models otherwise, including SRIM. The measured sputtering yields for 30 keV, 40 keV and 50 keV Ar are close to the values predicted by the Matsunami formula using 2.17 eV for the Bi surface binding energy, and higher than the values obtained from SRIM. Differences between the measured $Y$ and those obtained from SRIM may be attributed in part to the fact that the Bi surface binding energy changed with time during the experiment as the beam roughened the surface. Discrepancies between the
Figure 1.12. Plot of simulated [SRIM] and fitted [using Eq. (41)] differential sputtering yield (atoms/steradian-ion) vs. polar angle (degrees) for 10 keV, 30 keV and 50 keV Ar on Bi. Approximately 168,000, 184,000 and 180,000 sputtered atoms were analyzed for 10 keV, 30 keV and 50 keV Ar on Bi, respectively.

Present experimental results and atleast two of the models (theoretical [17] and simulation) may be attributed in the part to the fact that these models are for the low fluence limit (zero fluence) whereas the present experimental results were obtained for the fairly high fluence of $\sim 3.1 \times 10^{20}$ atoms/cm$^2$. At this high fluence, composition modification is inevitable, and can lead to changes in the sputtering yield through dilution of the original material and through changes in the value of the surface binding energy, which has a strong affect on the sputtering yield. Also, the yield could have been affected by the development of the surface topography (roughening) with the high bombarding fluence.
Table 1.2. Sputtering yield $Y$ (atoms/ion) as a function of energy for normally incident Ar$^+$ ions on a solid Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown.

1.6. Summary

In this study we have determined the angular distributions and total yields of atoms sputtered from the surface of the heaviest stable element, Bi, by normally incident 10 keV – 50 keV Ne$^+$ and Ar$^+$ ions, determined both experimentally and by Monte Carlo computer simulation. The sputtering yields and the measured angular distributions of the sputtered atoms for these target-ion combinations have not been reported previously, to our knowledge, and add to the very sparse experimental sputtering database for Bi. Our experimental results also support the conclusion that the shape of the sputtering angular distribution for normally incident projectiles on a polycrystalline target can depend on projectile species and energy in the linear cascade regime. The measured sputtering yield was found to increase with
Figure 1.13. Plot of sputtering yield $Y$ (experiment) vs Ar$^+$ ion energy $E$ compared to sputtering yield values predicted by Sigmund’s theory, the empirical formula of Matsunami et al., and values obtained from the SRIM code. Sputtering yield values obtained by using the Bi surface binding energy predicted by Kudriavtsev et al. with Sigmund’s theory and the empirical formula of Matsunami et al. are also shown.

For normally incident 10 keV Ne$^+$ on Bi, the measured sputtering yield was lower than values predicted by all the models used for comparison. The measured yield for 50 keV Ne$^+$ on Bi was found to agree with the value obtained from SRIM simulation. No comparison with other experimental results for Ne on Bi could be made because of a lack of published data. The measured sputtering yield for normally incident 10 keV Ar$^+$ on Bi was close to the values obtained from theoretical and semi-empirical models when using the value of the surface binding energy for sputtered
atoms from a model described in [47]. The measured sputtering yields for 30 keV – 50 keV \(\text{Ar}^+\) on Bi were close to values predicted by the semi-empirical formula of [18]. Generally good agreement was found between experiment and simulation for the shapes of the angular distributions of sputtered Bi atoms, which were found to be over-cosine. For the projectile energy range sampled the shape of the sputtering angular distribution due to \(\text{Ar}\) on Bi, for which the target-to-projectile mass ratio \(M_T/M_I\) is \(\sim 5\), showed no significant dependence on projectile energy. However, for \(\text{Ne}\) on Bi, for which \(M_T/M_I\) is \(\sim 10\), the sharpness of the measured sputtering angular distribution was found to increase with increasing projectile energy, suggesting an increase contribution to the sputtering yield from the deeper layers as bombarding energy increased.
CHAPTER 2

ANGULAR NON-STOICHIOMETRIC SPUTTERING YIELD OF INHOMOGENEOUS ALLOY

2.1. Introduction and Motivation

When a target is bombarded by projectile atoms there is always a possibility of the accumulation of the projectile atoms in the target material, which will eventually change the target composition. Thus, because of the accumulation of the sputtering species, experimental studies are actually rarely performed on pure mono-atomic target materials. Generally, a decrease in the sputtering yield of the original target material is often observed due to implanted ions; however the yield may also increase if the ions form a volatile compound with the target atoms. Knowledge and understanding of overall sputtering yields of multi-component materials are important since such materials are used in many practical situations where sputtering is employed. Researchers have been trying to understand the detailed phenomenon of the sputtering of multi-component materials for the past four decades. One of the first analytical models, based on different sputtering yields of different components, for explaining the compositional changes due to ion bombardment was presented by Patterson and Shinn [48]. Experimental data related to the sputtering of multi-component materials before the late 1960s were controversial due to the lack of sensitive surface composition analysis methods. However, after techniques like Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS) became available, measurement of the composition of the surface or collected material was feasible. Andersen et al. [49] made an important step in understanding the processes leading to the differences in the angular distributions of the components sputtered from an alloy. In that study they measured the angular distribution of sputtered Cu and Pt atoms from CuPt targets. A strong Cu segregation to the surface during Ar ion bombardment was observed. Since then measurements have been performed on a number of alloys [29, 50, 51, 52, 53, 54]; however, the Bi:Ga alloy, the sputtering of which has not previously been investigated, ex-
hibits even more pronounced surface segregation [19] than any of the other alloys previously studied. Gibbsian segregation modifies the concentrations of alloy components at surfaces and interfaces so that the surface free energy is minimized. The weakly bound species segregates to the surface and also tends to sputter preferentially. The angular distributions of the individual sputtered species are affected by the compositional gradients within the depth of origin of sputtered atoms. Hence the existence or non-existence of an altered layer of the order of the sputtered depth in a given system can be identified most directly by measuring angular distribution of sputtered atoms [46]. The differential properties of alloy sputtering are affected by pronounced changes of alloy composition in the near surface region, which makes the sputter depth or the depth of origin of sputtered atoms an important parameter. Both Gallium (Ga) and Bi are low melting-points metals, with Bi melting at 271 °C and Ga melting just above room temperature. Bi and Ga coexist in the liquid phase at ∼30 °C [55]. The low vapor pressures of Ga and Bi make them UHV compatible, which is an important quality when working with ion beams and studying surfaces. The low vapor pressure makes Bi alloys suitable not only for Liquid Metal Ion Sources (LMIS) [9, 56] for conventional FIB systems but also a potential candidate for single-column dual focused ion/electron beam systems [57]. Gibbsian segregation at the surface of the Ga:Bi alloy with bulk composition of 0.2 atomic % Bi and 99.8 atomic % Ga results in an extreme concentration ratio gradient in the surface atomic layers, making it an ideal target to study non-stoichiometric sputtering [58, 19]. The liquid Ga:Bi alloy had been considered to form an almost complete Bi monolayer atop a bulk of essentially pure Ga [58, 19]. Consequently, this material offers an opportunity to measure the effects of the depths of origin of sputtered atoms under the cleanest and least ambiguous conditions yet. That it is a liquid target also obviates the fluence dependence of sputtering; the sputtering yield remains unchanged with fluence because the concentration remains constant due to high atomic mobility. Due to this self-repairing property the target remains atomically smooth and the composition profile is maintained during the sputtering process.

This chapter reports the experimental and simulational study of the angular distri-
butions of Bi and Ga atoms sputtered by normally incident 25 keV and 50 keV Ar+ ions from the surface of a Bi:Ga alloy. The partial sputtering yields obtained from the angular distributions are also reported. Angular distributions of sputtered atoms and the overall sputtering yield for elemental liquid Ga targets are also presented. Effects of target surface segregation on the angular distributions and sputtering yields are discussed.

2.2. Theory

According to reviews [59, 60], the phenomenon of sputtering of multi-component targets is commonly specified either by means of measurements of the flux of the sputtered atoms or of the composition of the target, which involves measuring the differential sputtering yield in the former case and concentration profile in the latter. The partial sputtering yield $Y_i(E, \Omega, \phi) \, dE \, d^2\Omega$ is defined as the average number of $i$-atoms per incoming ion sputtered into a solid angle $d^2\Omega$ in the direction $\Omega$, in the energy interval $dE$ around energy $E$. $Y_i$ is measured as a function of bombarding ion beam characteristics and fluence $\phi$ (ions per area) and is expressed as [46],

\begin{equation}
Y_i(\phi) = \int_0^\infty dx \sigma_i(x) N_i(x, \phi),
\end{equation}

where the concentration profile, $N_i(x, \phi)$ is defined as the mean number of $i$-atoms per unit volume at depth $x$ beneath the bombarded surface after a bombarding ion fluence $\phi$. Also,

\begin{equation}
\sigma_i(x, z) = \int_{-\infty}^{-x} d\sigma_i(x, z),
\end{equation}

provided that the surface is located at $x = 0$. Here, $d\sigma_i(x, z)$ is the relocation cross section and is defined so that $\delta\phi d\sigma_i(x, z)$ is the probability for an $i$-atom at depth $x$ to be relocated collisionally to a depth $(x+z, dz)$ after a fluence $\delta\phi$. The relocation cross section (Eq. 44) for recoil implantation and the isotropic cascade mixing are described in detail in [61]. If the sputtering cross section $\sigma_i$ is the same for all $i$ then the sputtering process is called stoichiometric, and if the $\sigma_i$ are different for different $i$ then it is referred to as non-stoichiometric, or preferential, sputtering.
When a multi-component target is sputtered, the sputtering process can be divided into primary and secondary sputter effects [62, 63]. The processes leading to non-stoichiometries in the sputtered flux even from a homogeneous target are classified as primary process. Secondary processes are those occurring in the target only after prolonged bombardment by the energetic projectiles. The linear collision cascade theory can be applied to primary sputtering processes such as preferential sputtering [59]. Prolonged bombardment eventually leads to a stationary state, which means the concentration profile and sputtered flux become independent of the fluence. Above all, measuring the angular distribution of sputtered particles produces a very convenient means to identify the existence or non-existence of an altered layer with respect to the sputtered depth. Hence, it becomes very important to correlate the depth of origin of sputtered atoms with the angle of ejection. Consider a target with atoms of atomic number $Z_i$, mass $M_i$, and abundance $\alpha_i$, for $i = 1, 2, 3, ...$ such that

\begin{equation}
\sum_i \alpha_i = 1.
\end{equation}

Let the cross-section for elastic collisions between the atoms be $d\sigma_{ij}(E, T) = (d\sigma_{ij}/dT)dT$, where $E$ is the energy of the $i$-atom colliding with a $j$-atom at rest, and $T$ the recoil energy of the $j$-atom. Consider the standard power law approximation for the cross section as in Eq. (3) [21],

\begin{equation}
d\sigma_{ij}(E, T) = \begin{cases}
C_{ij}E^{-m}T^{-1-m} & \text{when } 0 \leq T \leq \gamma_{ij}E \\
0 & \text{otherwise}
\end{cases}
\end{equation}

where $m$ is a number characterizing the screened Coulomb interaction potential between colliding atoms, with $0 \leq m \leq 1$ [21];

\begin{equation}
\gamma_{ij} = \frac{4M_iM_j}{(M_i + M_j)^2};
\end{equation}

and

\begin{equation}
C_{ij} = \begin{cases}
\frac{\pi}{2}\lambda_m a_{ij}^2 \left( \frac{M_i}{M_j} \right)^m \left( \frac{2Z_i e^2}{a_{ij}} \right)^{2m}, & m > 1/4 \\
\frac{\pi}{2}\lambda_m a_{ij}' \left( \frac{M_i}{M_j} \right)^m (2A_{ij}')^{2m}, & m \leq 1/4.
\end{cases}
\end{equation}
Here,

\[ a_{ij} = 0.885a_0(Z_{i}^{2/3} + Z_{j}^{2/3})^{-1/2}, \]

\[ a'_{ij} = 0.219\text{Å}, \]

\[ A'_{ij} \simeq 52(Z_{i}Z_{j})^{3/4}\text{eV}, \]

\( \lambda_m \) is as specified in Eq. (4) in section 1.2.1, \( a_0 = 0.529 \text{ Å} \) and \( e \) is the elementary charge. With this, the following result was obtained for the ratio of particle fluxes at energy \( \epsilon \) in a binary, infinite, random medium \[64, 65\]:

\[ \frac{\text{flux}_1}{\text{flux}_2} = \frac{N_1}{N_2} \frac{S_{21}(\epsilon)}{S_{12}(\epsilon)}, \]

where \( S_{ij} \) is the stopping cross section of an \( i \)-atom interacting with \( j \)-atoms:

\[ S_{ij}(E) = \frac{1}{1 - m} C_{ij} \gamma_{ij}^{1-m} E^{1-2m}. \]

Eq. (53) was also derived from a principle of detailed balance in the collision cascade where the flux of energy from the subsystem of \( i \)-atoms to the subsystem of \( j \)-atoms equals the opposite flux \[66\]. Since screened-Coulomb interaction potentials are symmetric in \( i \) and \( j \), the factor \( S_{21}(\epsilon)/S_{12}(\epsilon) \) is independent of the atomic number. Non-stoichiometry stems from a kinematic factor which, in the power law approximation, reads

\[ \frac{S_{21}(\epsilon)}{S_{12}(\epsilon)} = \left( \frac{M_2}{M_1} \right)^{2m}. \]

For a monoatomic medium, the energy integrated particle flux is known to be \( \propto U^{2m-1} \) where \( U \) is the surface binding energy. This finding translates into a \( U_i^{2m-1} \) dependence of the partial sputtering yield of the \( i \)-th component in a random polyatomic target. To summarize, the simplified transport theory predicts the following ratio of the partial sputter yields in a homogeneous binary medium:

\[ \frac{Y_1}{Y_2} = \frac{N_1}{N_2} \left( \frac{M_2}{M_1} \right)^{2m} \left( \frac{U_2}{U_1} \right)^{1-2m}. \]
2.3. Simulation Environment

Computer simulations were performed with the SRIM code. Ions interacting with target atoms every monolayer were desired; hence, monolayer collision steps were selected over the free flight path approximation in the simulations. To ensure that there were no transmitted atoms contributing to the sputtering yield, 220 nm thick Ga and Ga:Bi targets were chosen after several trial simulations for normally incident Ar ion bombardment. To incorporate the Gibbsian segregation in the Ga:Bi alloy, the target was specified to have a monolayer coverage of Bi atoms, and the bulk was pure Ga. The value of the mean atomic spacing, $\lambda_0 = N^{-1/3}$, where $N$ denotes the number density of the target atoms, was a convenient choice for the thickness of the monolayer. The heats of sublimation of Bi and Ga, equal to 2.2 eV and 2.8 eV, respectively, were used in calculations as the values of the surface binding energies. For 50 keV Ar on Ga, approximately 493,000 sputtered Ga atoms were analyzed for angular distribution measurements. Approximately, 129,000 sputtered Ga atoms and 285,000 sputtered Bi atoms were analyzed for 25 keV Ar on Ga:Bi alloy. During the simulation, the polar and the azimuthal angles of the sputtered atoms’ traveling directions were documented as well. The ejection angles were collected into multiple polar angle bins each with a size of $5^\circ$, and the counts were normalized by dividing by the number of Ar projectiles to obtain the sputtering yield differential in angle.

2.4. Experiment

2.4.1. Sample Preparation

The Ga:Bi alloy was prepared by mixing 0.29 g of Bi shot (99.9999% pure, Cominco Electronic Materials) with 53.3 g of Ga (99.9999% pure, Eagle-Picher Industry, Inc.) under an Ar gas environment in a glove bag. The masses of the materials were measured using an Acculab precision analytical balance. The mixing was effected in a glass beaker at $\sim 90^\circ$C on a Thermolyne® heating stir plate for $\sim 3$ hours. The surface of the liquid sample was mechanically swept after transfer to the target holder to remove any macroscopic oxide layer. The target was then transferred into the load lock connected to the UHV chamber.
and the load lock was evacuated. After the target solidified, it was transferred from the load lock into the UHV chamber. Similar measures were taken while preparing the liquid Ga target. A special target holder as seen in Fig. 2.1 to hold the liquid target with an exposed vertical face was designed for this experiment. Liquid Ga and liquid Ga:Bi alloy were held in place due to the structure of the target holder as well as the surface tension of the liquid target itself. The volume of the target holder was $\sim 0.7 \text{ cm}^3$, and $> 0.5 \text{ cm}^3$ of liquid metal (alloy) was in the target holder during sputtering. The fractional depletion of Bi after the longest sputtering duration was estimated to be $< 4\%$.  

Figure 2.1. Photograph of the target holder in the UHV chamber with the liquid Ga:Bi binary alloy target. During sputtering the bulge on the target was flush with the edge of the collector holder assembly, and the offset from the foil center of curvature was accounted for with the fitting parameter $F$ for angular distribution calculations.
2.4.2. Sputtering

Sputtering of liquid Ga:Bi alloy was carried out by using normally incident 25 keV and 50 keV Ar\(^+\) ions produced from the Cockcroft Walton accelerator. Details of the experimental setup are provided in Chapter 1. To maintain the target temperature, which was set at 40 °C, a controller was employed which used feedback from a thermocouple to control the current through the target heater. A spot on a target was sputtered clean for \(\sim 30\) min to avoid collection of any contamination on the target surface and to ensure that an atomically clean target surface was obtained as surface contamination can alter the angular distribution of sputtered atoms. The target was then heated to 100 °C for 30 min and was then cooled to 40 °C and sputtered again. The entire liquid Bi:Ga target was cleaned by four sequences of Ar ion bombardment followed by temperature cycling. We observed the migration and disappearance of surface impurities lying outside the sputtered area, and hence were confident of having cleaned the entire target surface area. This behavior has previously been reported by others [67, 68]. A different collector holder was rotated into place after the sputter cleaning process and was used to collect the sputtered atoms for the actual measurements. The target was sputtered with an integrated charge of \(\sim 60\) mC. For the above mentioned purposes, normally incident 25 keV and 50 keV Ar\(^+\) beams of \(\sim 450\) nA and diameter of \(\sim 200\) \(\mu\)m were used.

2.5. Results

2.5.1. Sputtering of Liquid Ga

The areal density of the sputtered Ga atoms on the collector foil was extracted by RBS. A 4.5 MeV Si\(^+2\) beam produced by the SNICS-II and the IBMAL’s 9SDH-2 accelerator was used for these purposes. The experimental set up for RBS and the methods for accurate current integration used for the collector foil analysis are described in detail in Appendix C. The conversion of these areal densities to differential yield is discussed in Chapter 1 and Appendix B. Fig. 2.2 shows a plot of measured and fitted [using Eq. (41)] differential sputtering yield vs. polar angle in the sputtering geometry for normally incident 50 keV Ar\(^+\)
on liquid Ga. The values of the fitting parameters with their uncertainties are provided in Table. 2.1.

![Figure 2.2](image.png)

**Figure 2.2.** Plot of measured and fitted [using a modification of Eq. (41) as described in Appendix A] differential sputtering yield of Ga as a function of polar angle for normally incident 50 keV Ar\(^+\) on liquid Ga.

The over-cosine shape \((B = 1.9)\) is typical of that observed for other materials, both experimentally and by computer simulation. However, the linear cascade theory cannot address this detail of the distribution as it assumes an isotropic flux of low energetic recoils beneath the surface, and hence always predicts a cosine distribution \([B = 1]\) of sputtered atoms. It has been suggested in the past by [69, 70, 71] that the over-cosine distribution could be due to the anisotropy of the recoil-atom motion within the target. Fig. 2.3 shows the simulated and fitted [using Eq. (41)] differential sputtering yields for 50 keV Ar on Ga. The values of the fitting parameters are provided in Table. 2.1. It appears from Fig. 2.3
that the differential sputtering yield from $-15^\circ$ to $+15^\circ$ is not fitted properly by Eq. (41). However, these points do not contribute significantly to the overall yield when one integrates over the solid angle $d\Omega$, given by

$$d\Omega = \sin \theta d\theta d\phi.$$  

Figure 2.3. Plot of simulated and fitted [using Eq. (41)] differential sputtering yield of Ga as a function of polar angle for normally incident 50 keV Ar on Ga.

Fig. 2.4 is similar to Fig. 2.3, although this time, the distribution is also weighted by the solid angle factor $\sin \theta$ to show the relative importance of the various regions of the distribution to the overall yield. The overall yield is insensitive to the fit in the region closest to the target normal. Also, the difference between the overall sputtering yield from the simulation and the yield calculated from the fit to the simulated data is $\sim2\%$. It is found that the total sputtering yield $Y$ from the simulation is $\sim18\%$ higher than the experimental
Figure 2.4. Plot of simulated and fitted [using Eq. (41)] differential sputtering yield of Ga as a function of polar angle for normally incident 50 keV Ar on Ga. The shaded distribution is weighted by the solid angle factor $\sin \theta$, to demonstrate the relative importance of different regions of the distribution to the total sputtering yield.

value, well within the limitations of the simulation environment. There is no report (to our knowledge) on the sputtering angular distribution or the total sputtering yield of a pure liquid Ga target, hence no independent comparison could be made. We attribute this $\sim 18\%$ difference in the over-all sputtering yield to the following limitations in the simulation environment:

- lack of experimental data for the inelastic energy loss, and
- uncertainty in the value of the surface binding energy, which is one of the major factor that governs the overall sputtering yield.
<table>
<thead>
<tr>
<th>Ion−Energy Pair</th>
<th>Methodology</th>
<th>$A$ (atoms/steradian-ion)</th>
<th>$B$ (atoms/ion)</th>
<th>$Y$ (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 keV Ar</td>
<td>Expt</td>
<td>1.82 ± 0.10</td>
<td>1.87 ± 0.03</td>
<td>3.98 ± 0.23</td>
</tr>
<tr>
<td>50 keV Ar</td>
<td>Simulation</td>
<td>3.05 ± 0.04</td>
<td>2.90 ± 0.04</td>
<td>4.91 ± 0.08</td>
</tr>
</tbody>
</table>

Table 2.1. Sputtering yield $Y$ (atoms/ion) for normally incident 50 keV Ar ions on Ga. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown.

The angular distribution of sputtered Ga atoms for 50 keV Ar from simulation is found to be extremely over-cosine [$B = 2.9$] as compared to the present experimental value [$B = 1.9$].

2.5.2. Sputtering of Liquid Ga:Bi

Fig. 2.5 shows plots of the differential partial sputtering yield of Bi vs. polar angle $\theta$ for 25 keV Ar$^+$ on the liquid Ga:Bi alloy. Bi$_{\text{ME}}$ and Bi$_{\text{SE}}$ are the notations for the differential partial sputtering yield of Bi obtained from areal density measurements by RBS analysis using the mean energy approximation and surface energy approximation, respectively. The former was introduced to correct for the thickness of the sputtered material on the collector foil. The areal density of Bi atoms on the collector foil when measured using the surface energy approximation ranged from $\sim 6.8 \times 10^{15}$ atoms/cm$^2$ to $\sim 1.0 \times 10^{17}$ atoms/cm$^2$. The difference in the measured areal density of the foil between the surface energy approximation and mean energy approximation for the thickest spot on the collector foil was found to be $\sim 2.2\%$. It is also clear from Fig. 2.5 that this difference has no effect on the shape of the angular distribution of sputtered atoms and the effect on the overall sputtering yield is < 1%.

Fig. 2.6 shows a plot of differential partial sputtering yield vs. polar angle in the sputtering geometry for 25 keV Ar$^+$ on the liquid Ga:Bi binary alloy. Here the angular distributions obtained from collector foil analysis are not corrected for the offsets in the sputtering geometry discussed in Appendix A in detail.
Figure 2.5. Plot of measured Bi differential partial sputtering yield (atoms/steradian-ion) vs. polar angle $\theta$ (degrees) for 25 keV Ar$^+$ on Ga:Bi alloy. Bi$_{\text{ME}}$ and Bi$_{\text{SE}}$ are the differential sputtering yields of Bi obtained from the RBS analysis of the areal densities by means of the mean energy approximation and surface energy approximation, respectively.

Figs. 2.7 and 2.8 show plots of measured and simulated differential partial sputtering yields, respectively, of Ga and Bi atoms for 25 keV Ar$^+$ on Ga:Bi. The values of the fitting parameters for experiment and simulation are provided in Table 2.2. The areal densities on the collector foil used to obtain the measured differential partial sputtering yields ranged from $\sim 6.8 \times 10^{15}$ atoms/cm$^2$ to $\sim 1.1 \times 10^{17}$ atoms/cm$^2$ for Bi and from $\sim 6.4 \times 10^{15}$ atoms/cm$^2$ to $\sim 5.4 \times 10^{16}$ atoms/cm$^2$ for Ga. It is observed that the angular distribution of sputtered Ga atoms is over-cosine in nature for both experiment and simulation. However the degree of over-cosiness is different and is evident in Figs. 2.7 and 2.8 and in Table 2.2. The Monte Carlo based TRIM code which predicts a value of $B = 2.6$ for Ga, underestimates
Figure 2.6. Plots of measured and fitted [using a modification of Eq. (41) as described in Appendix A] differential partial sputtering yield (atoms/steradian-ion) vs. polar angle $\theta$ (degrees) for 25 keV Ar$^+$ on liquid Ga:Bi. The distributions are as-measured, without removing the effects of misalignments in sputtering geometry described in Appendix A.

The experimentally observed value of $B = 3.4$.

The ranges of normally incident 25 keV and 50 keV Ar$^+$ in Ga are $\sim 250$ Å and $\sim 400$ Å, respectively [42]; hence, most of the primary collisions will occur too deep inside the target for the recoil atoms to backscatter and still make it out of the target. Thus, reflective collision sputtering, which takes place when the primary collision between the incident ion and the target atom occur close to the surface, is not the reason for these over-cosine distributions.

As predicted by multicomponent sputtering theory [46] and observed experimentally [28, 59], for such a binary system the surface depletion of one species leads to preferential ejection of that species closer to the surface normal and vice versa for the enriched species.
Figure 2.7. Plots of measured and fitted [using a modification of Eq. (41) as described in Appendix A] differential partial sputtering yields of Ga and Bi atoms as a function of polar angle for normally incident 25 keV Ar$^+$ on liquid Ga:Bi. Relative uncertainties for the measured values were due to counting statistics in the RBS analysis, and ranged from $\sim 0.2\% \pm 1\sigma$ near $0^\circ$ to $\sim 5.0\%$ near $-90^\circ$.

Experimentally, we have observed here a similar effect in the Ga:Bi binary alloy where the surface is enriched in Bi atoms. From Fig. 2.7 and Table 2.2 it is seen that the Bi atoms are preferentially ejected far from the surface normal and the distribution of Ga atoms originating from underneath the surface layer is sharply peaked towards the surface normal as compared to the distribution of Bi atoms originating from the surface. The values of the over-cosine parameter of Bi and Ga for 25 keV Ar$^+$ are $B = 1.8$ and 3.4, respectively.

In the simulation environment, Ga atoms in the second layer were physically blocked by a layer of Bi atoms. The simulated partial sputtering yield of Ga for 25 keV Ar on
Ga:Bi alloy is $\sim$58% higher than the one obtained from experiment in the present study. This difference is due to the difference between the shapes of the distributions and the simulated differential partial sputtering yield amplitudes $A$, for which the simulated value is $\sim$29% greater than the experimental value (within the approximations of the simulation). The angular distribution of sputtered atoms is dictated by surface phenomena; hence it is inferred that the last collision(s) in the Ga depleted surface is(are) not treated properly in the MC based TRIM code, as it produces a broader distribution of Ga as compared to the experimental result. The simulated partial sputtering yield of Bi for 25 keV Ar on Ga:Bi alloy is $\sim$8% lower than one obtained from experiment in the present study, although the simulated fitting parameter $B$ is 85% larger than the experimental value. Hence, the simulation is predicting the Bi partial sputtering yield to an acceptable level of uncertainty;
Table 2.2. Experimental and simulated value of partial sputtering yield \( Y_i \) (atoms/ion) for normally incident 25 keV Ar ions on Ga:Bi. Values for fitting parameters \( A \) and \( B \) along with their uncertainties are also shown.

<table>
<thead>
<tr>
<th>Ion–Energy Pair</th>
<th>Methodology</th>
<th>Element</th>
<th>( A )</th>
<th>( B )</th>
<th>( Y_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 keV Ar</td>
<td>Expt</td>
<td>Ga</td>
<td>0.69 ± 0.04</td>
<td>3.39 ± 0.12</td>
<td>0.99 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi</td>
<td>1.65 ± 0.11</td>
<td>1.79 ± 0.11</td>
<td>3.71 ± 0.29</td>
</tr>
<tr>
<td>25 keV Ar</td>
<td>Simulation</td>
<td>Ga</td>
<td>0.89 ± 0.00</td>
<td>2.57 ± 0.02</td>
<td>1.56 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi</td>
<td>2.35 ± 0.02</td>
<td>3.31 ± 0.07</td>
<td>3.42 ± 0.07</td>
</tr>
</tbody>
</table>

Figure 2.9. Plots of normalized differential fitted sputtering yields of Ga and Bi for 25 keV Ar on Ga:Bi: (a) measured and (b) simulated.

Fig. 2.9 shows plots of the experimental and simulated normalized differential fitted sputtering yields of Ga and Bi for 25 keV Ar on Ga:Bi. Fig. 2.9(a) represents the experimental plot and it is observed that the Bi atoms originating from the surface monolayer
are preferentially ejected in directions away from the surface normal compared to the Ga, which is in support of the theory and the results for previously measured solid and liquid targets. Fig. 2.9(b) represents the normalized simulated differential sputtering yields for Bi and Ga. In contrast to the theory, and previous and present experimental results, the TRIM simulation predicts a flatter angular distribution \([B = 2.6]\) for the element originating from underneath the surface monolayer (Ga) and sharper angular distribution \([B = 3.3]\) for the element originating from the surface monolayer (Bi). For 25 keV Ar on Ga:Bi binary alloy the partial sputtering yield of Ga is lower than that of Bi and the angular distribution is much sharper. Bi follows a \(\cos^{1.8}\theta\) function and Ga follows \(\cos^{3.4}\theta\) function from the experimental results. From the simulation, Bi follows a \(\cos^{3.3}\theta\) function and Ga follows a \(\cos^{2.6}\theta\) function.

The measured differential partial sputtering yields and the fitted functions for 50 keV Ar\(^+\) on the Ga:Bi binary alloy are plotted in Fig. 2.10. The areal densities on the collector foil used to obtain the measured differential partial sputtering yield ranged from \(\sim 9.8 \times 10^{14}\) atoms/cm\(^2\) to \(\sim 9.2 \times 10^{16}\) atoms/cm\(^2\) for Bi and from \(\sim 2.1 \times 10^{14}\) atoms/cm\(^2\) to \(\sim 4.5 \times 10^{16}\) atoms/cm\(^2\) for Ga. Again, the Bi atoms originating from the surface were preferentially sputtered in the direction away from the target normal and Ga atoms originating from the layer underneath the Bi monolayer were preferentially sputtered into a narrow cone towards the target normal. From Fig. 2.10 and Table. 2.3, Bi follows a \(\cos^{1.6}\theta\) function and Ga follows a \(\cos^{3.6}\theta\) function for 50 keV Ar\(^+\) on Ga:Bi from experimental results.

Hence, as compared to 25 keV Ar on Ga:Bi data, it is observed that the angular distribution for the Ga atoms becomes even sharper and the angular distribution of the Bi atoms broadens. The anisotropy of the recoil-atom motion within the target responsible for the over-cosine distribution seems to be more extreme for normally incident 50 keV Ar\(^+\) on Ga:Bi than for 25 keV Ar\(^+\).

In the present study, measurements were made for normally incident 50 keV Ar\(^+\) on liquid Ga, hence some comments can be made about the depth of origin of sputtered atoms. It is well known that most of the sputtered atoms originate from the first few monolayers.
Figure 2.10. Plots of measured and fitted [using a modification of Eq. (41) as described in Appendix A] differential partial sputtering yields of Ga and Bi for normally incident 50 keV Ar\textsuperscript{+} on liquid Ga:Bi. Relative uncertainties for measured value were due to counting statistics in the RBS analysis, and ranged from \sim0.2\% (\pm1\sigma) near 0\textdegree to \sim6.3\% near 90\textdegree.

If we assume that the replacement of the surface monolayer of Ga with Bi doesn’t affect the yield of Ga from beneath the surface, then $F_1$, the fraction of atoms originating from the surface monolayer is given as:

$$F_1 = 1 - \frac{Y_{\text{Ga}_2}}{Y_{\text{Ga}_1}},$$

where $Y_{\text{Ga}_1}$ and $Y_{\text{Ga}_2}$ are the Ga sputtering yields for normally incident 50 keV Ar\textsuperscript{+} on Ga and Ga:Bi, respectively. Hence, if we assume a monolayer coverage of Bi atoms atop Ga in the Ga:Bi alloy as suggested by Lei et al. [19], then \sim80\% of sputtered atoms are originating from the surface monolayer for the Ga target.
<table>
<thead>
<tr>
<th>Ion–Energy Pair</th>
<th>Methodology</th>
<th>Element</th>
<th>$A$ (atoms/steradian-ion)</th>
<th>$B$ (atoms/ion)</th>
<th>$Y_i$ (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 keV Ar</td>
<td>Expt</td>
<td>Ga</td>
<td>0.61 ± 0.04</td>
<td>3.64 ± 0.10</td>
<td>0.83 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi</td>
<td>1.25 ± 0.08</td>
<td>1.55 ± 0.09</td>
<td>3.08 ± 0.22</td>
</tr>
<tr>
<td>50 keV Ar</td>
<td>Simulation</td>
<td>Ga</td>
<td>0.78 ± 0.01</td>
<td>2.66 ± 0.04</td>
<td>1.34 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi</td>
<td>1.90 ± 0.03</td>
<td>3.08 ± 0.05</td>
<td>2.92 ± 0.06</td>
</tr>
</tbody>
</table>

Table 2.3. Experimental and simulated value of partial sputtering yield $Y_i$ (atoms/ion) for normally incident 50 keV Ar ions on Ga:Bi. Values for fitting parameters $A$ and $B$ along with their uncertainties are also shown.

Generally, the value of 75% - 95% for the contribution from the surface monolayer has been predicted by computer simulations [72]. Here, Kelly and Oliva had proposed that $\bar{x}$, the mean depth of origin of sputtered atoms, can be written as:

\begin{equation}
\bar{x} = [0.8 \pm 0.1] \cdot \lambda_0,
\end{equation}

where $\lambda_0$ is the mean interatomic distance in the target. However, Shulga and Eckstein have suggested that the error $\pm 0.1$ in Eq. (41) strongly underestimates the actual spread of experimental and simulation data and must be replaced by $\pm 0.25 \ (\pm 1\sigma)$ [73]. In their computer simulation study of depth of origin of sputtered atoms for elemental targets [73], Shulga and Eckstein found that the $\bar{x}$ is a function of atomic density, projectile energy, the angle of incidence, and projectile and target atomic numbers. For these studies they used the Monte Carlo program TRIM.SP [74, 75] and the lattice code OKSANA [76, 77, 78]. It was found that for Ga atoms, $\bar{x} = 3$ Å for 10 keV normally incident Ar.

Recently, Wittmack and Mutzke have attempted to understand the dependence of the depth of origin of sputtered atoms on target properties such as surface binding energy to identify the correlation in low projectile-energy ranges [79]. Here, the sputtering yields differential in depth and ranges of recoil atoms were calculated using the Monte-Carlo sim-
ulation code SDTrimSP [80]. It was argued that the distribution of the depth of origin is determined by the range of recoil atoms set in motion in the direction of the surface. It was found that 98% to 75% of sputtered atoms originated from the outermost layer, for impact energies between 40 eV and 10 keV.

![Figure 2.11](image) **Figure 2.11.** Plots of simulated and fitted [using Eq. (41)] partial differential sputtering yields of Ga and Bi for normally incident 50 keV Ar on Ga:Bi.

Hubbard et al. [50] measured the angular distributions of sputtered atoms from a Ga-In eutectic alloy for normally incident 3 keV, 25 keV and 50 keV Ar$^+$ ions. Here they used the measured composition profile of the alloy surface and composition of the sputtered flux to calculate the fraction of sputtered atoms originating from the first atomic layer. It was found that 94% of sputtered atoms for 3 keV Ar bombardment originated from the outermost layer and 87% of sputtered atoms for 25 keV and 50 keV Ar bombardment originated from the outermost layer. Angular distributions for pure elemental targets were not obtained,
specifically for Ga.

![Figure 2.12](image.png)

**Figure 2.12.** Plots of normalized differential fitted sputtering yields of Ga and Bi for 50 keV Ar on Ga:Bi: (a) measured and (b) simulated.

The differential angular sputtering yields as a function of angle $\theta$ obtained from our simulation study of 50 keV Ar on Ga:Bi binary alloy are plotted in Fig. 2.11. It is found that the angular distribution of sputtered atoms for Bi is sharper than that for Ga atoms in the present simulation, as Bi follows a $\cos^3 \theta$ distribution and Ga follows a $\cos^{2.7} \theta$ distribution. The simulated partial sputtering yield of Ga for 50 keV Ar on Ga:Bi alloy is $\sim 61\%$ higher than the one obtained from experiment in the present study. This large difference is attributed to the uncertainty in simulation for calculating the differential partial sputtering yield amplitude $A$ along with underestimating the sharpness of the over-cosine distribution for Ga atoms. The simulated partial sputtering yield of Bi for 50 keV Ar on Ga:Bi alloy is $\sim 5\%$ lower than the one obtained from experiment in the present study. Fig. 2.12(a) and 2.12(b) shows plots of measured and simulated normalized differential fitted sputtering yields of Ga and Bi as a function of $\theta$ for 50 keV Ar on Ga:Bi, respectively.

Fig. 2.13 presents the ratio of the measured partial differential sputtering yields, $\frac{dY_{Ga}}{d\Omega} / \frac{dY_{Bi}}{d\Omega}$, as a function of angle $\theta$ for normally incident 25 keV and 50 keV Ar$^+$ on Ga:Bi. The effect of extreme Gibssian segregation has caused the ratio of the partial yields to
change by a factor of $\sim 2.5$ and $\sim 4.5$ as function of $\theta$ for 25 keV and 50 keV Ar$^+$ ion energies, respectively.

The surface composition was not measured directly for the liquid metal alloy used for these measurements. However, the procedures described in [19, 81] were followed to prepare the target material and great care was taken to ensure that the sample was free of contaminating oxide. Consequently, we are confident that the surface composition of essentially monolayer coverage of Bi atop Ga reported in [19, 81] was reproduced here.

2.6. Summary

In this study we have presented the angular distributions and total yields of Ga and Bi atoms sputtered from the surface of liquid Ga and a liquid Ga:Bi binary alloy, by normally incident 25 keV and 50 keV Ar$^+$ ions, determined both experimentally and by Monte Carlo computer simulation. The sputtering yields and the measured angular distributions of the sputtered atoms for these target-ion combinations have not been reported previously, to our knowledge, and add significantly to the experimental sputtering database for liquid targets like Ga:Bi exhibiting extreme Gibbsian segregation. The observations from the present study can be summarize as follows:

(1) Angular distributions obtained in this study are all over-cosine in nature [$B > 1$] in contrast to the assumption of the collision cascade theory [for which $B = 1$].

(2) The overall sputtering yield of Ga from simulations was found to be $\sim 23\%$ higher than one obtained from the experiment in the present study, within the limitations of the simulation environment.

(3) Results from the present experiment support the theory of sputtering of multicomponent materials [46], which correlates the depth of the origin of sputtered atoms with the angle of the ejection so that grazing angle are associated with shallow depth of origin. Hence, as observed here and qualitatively predicted by [46], the value of $B$ for Ga atoms originating from liquid Ga and a liquid Ga:Bi target increases from 1.9 to 3.6, respectively.
(4) Another important result is the poor agreement between the simulated and experimental values of $B$. The value of $B$ for Ga atoms originating from Ga and Ga:Bi targets in simulation, changes insignificantly from 2.9 to 2.7, respectively. Hence, it can be concluded that the MC simulation is insensitive to Gibsian segregation, as it shows no effect on the distributions of atoms originating from the surface monolayer and underneath the surface.

(5) As compared to experimental results, the MC simulation TRIM predicts the Bi partial sputtering yield within $\sim 8\%$ and $\sim 5\%$ for 25 keV and 50 keV Ar on Ga:Bi alloy, respectively.

(6) Assuming a monolayer coverage of Bi atoms atop bulk Ga in the Ga:Bi alloy [19, 81] and comparing the sputtering yields of Ga from liquid Ga and liquid Ga:Bi alloy, it is found that for 50 keV Ar on Ga, 80\% of sputtered Ga atoms originate from the surface monolayer.

(7) The ratio of the partial differential sputtering yields $\frac{dY_{Ga}}{d\Omega}/\frac{dY_{Bi}}{d\Omega}$ is observe to decrease by a factor of $\sim 2.5$ and $\sim 4.5$ as function of increasing $\theta$ for 25 keV and 50 keV Ar$^+$ ion energy, respectively, due to extreme surface segregation.
Figure 2.13. Angular variation of the sputtered-particle composition ratio $Y_{Ga}/Y_{Bi}$ for 25 keV and 50 keV Ar$^+$ bombardments.
3.1. Sputtering of Solid Bi and Future Work

In the present study sputtering of solid Bi was performed using normally incident keV Ne and Ar ions. Two important quantities, the sputtering yield \( Y \) and the angular distribution of sputtered atoms, were investigated experimentally and by computer simulation. The overall experimental values of \( Y \) for 10 – 50 keV Ar on Bi were found to be comparable to the values predicted by various models described in Chapter 1. It can be concluded that in the linear collision cascade regime for normally incident Ar on Bi, both experimental and simulation results for the angular distributions of sputtered Bi atoms are over-cosine in nature. The degree of over-cosiness was found to change insignificantly over the energy regime studied, suggesting the recoils (responsible for the over-cosine distribution) contributing to the overall sputtering yield are originating from approximately same depth in the target for all sampled-projectile energy. This deviation from the linear collision cascade theory’s prediction of a cosine distribution of sputtered atoms may be attributed to the anisotropy of the recoil-atom motion within the target. It was also found that the rate of increase of \( Y \) with the projectile energy in the present experimental study was steeper as compared to the rate predicted by the models. This may be associated with the very high bombarding ion fluence (\( \sim 10^{20} \) ions/cm\(^2\)) in the experimental case whereas the theoretical and simulation models are for low or zero bombarding fluences. For 50 keV Ne, where \( M_T/M_I \sim 10 \), good agreement was found between the simulation and present experimental results for the angular distribution of sputtered Bi atoms and for the value of \( Y \). However, for less energetic Ne on Bi (10 keV) it was found that the angular distribution of sputtered atoms was broader as compared to the 50 keV case and the overall yield was lower at least by factor of two. This suggests that the recoils contributing to the overall sputtering yield for 10 keV Ne on Bi are produced closer to the target surface as compared to the 50 kev Ne on Bi. The higher number of reflected ions from the target surface in case of 10 keV Ne
could be a possible reason of the lower sputtering yield as compared to 50 keV Ne, as the deposited energy density which controls the sputtering could be lower in case of 10 keV Ne on Bi. It is also suggested that the bombardment induced surface topography (pitting) and surface roughness could be one of the factors defining the last collisions important in the angular distribution of sputtered atoms. No comparisons to the other measurements were made due to the lack of the previous experimental results for both Ne and Ar on bulk Bi.

For future work, it is suggested to study the sputtering of a semi-metallic target like Bi in detail due to keV light ions [e.g., He and Ne] from low ($\sim 10^{15}$ ions/cm$^2$) to high ion beam fluence (or to the point where the sputtering yield saturates). Also, the surface topography could be monitored while sputtering by adding an electron microscope to the the sputtering chamber or carefully increasing the ion beam fluence and monitoring the effect of the ion dose on the target surface. We propose that for normally incident 1 keV - 50 keV He$^+$ ions on Bi, the angular distributions of sputtered atoms may range from under-cosine to over-cosine. The cosine distribution results from geometrical isotropy in the low energetic recoil-atoms near the target surface (for less energetic light ions) and geometrical anisotropy creates the over-cosineness of the angular distributions. The MC simulation code SDTRIM.SP [82], which combines the static version TRIM.SP[74] and dynamic version TRIDYN [83], can be used to incorporate the compositional changes in the target during ion bombardment and help extract the depth of origin of sputtered atoms from the simulation results.

3.2. Sputtering of Liquid Ga and Liquid Ga:Bi Alloy and Future Work

Liquid targets have an advantage over solid targets when it comes to sputtering behavior as the atomic mobility is high in liquids as compared to solids. Due to this high atomic mobility the target surface composition and structure is essentially static and hence the factor of the surface topography which changes the distribution of the sputtered atoms and the overall sputtering yield is eliminated. In present study the angular distributions of sputtered atoms and the sputtering yields of liquid Ga and liquid Ga:Bi alloy were investigated experimentally and by computer simulation. The angular distribution of Ga atoms sputtered from the surface of liquid Ga was found to be under-cosine in shape from experiment
and simulation results. However, the degree of the over-cosineness was found to be higher in case of simulation measurements. A striking disagreement was found between experimental and simulation study in case of the angular distributions of sputtered atoms originating from the liquid Ga:Bi alloy exhibiting extreme surface segregation. The present experimental results are consistent with previous experimental work done on Ga:In eutectic alloy exhibiting less pronounced surface segregation [28]. To summarize, both the previous and present experiments exhibit an angular distribution of sputtered atoms originating from underneath the surface monolayer to be sharply peaked in angle as compared to the atoms originating from the surface monolayer. The present simulation study using SRIM has produced contra-dictory results where the species originating from the surface monolayer is strongly peaked around the surface normal as compared to the one originating from underneath the surface monolayer. Since the last few collisions of the atoms in the target strongly determines the distribution of the atom after leaving the target surface, it could be concluded that the Monte-Carlo based SRIM code is not accurately predicting the last collisions of the atoms within the target. In general, it is assumed that Eq. 58 (Chap. 2, pg. 61) very well describes the depth of origin of sputtered atoms. It could be argued that most of the atoms contributing to the overall sputtering yield originating from the surface monolayer are less sharply peaked around the surface normal as compared to the atoms originating from underneath the surface monolayer. In the present study using Eq. (57) it was found that almost 80% of sputtered atoms are originating from the surface monolayer of the Ga target. It could be concluded that the overall yield predicted by the simulation is acceptable by considering the limitations of the simulation environment (discussed in Chapters 1 and 2); however, the details of the distributions of the sputtered atoms are not accurately predicted, at least in the case of the binary alloy.

For future work it suggested to employ a molecular dynamics simulation code where atoms undergoing collisions are allowed to interact more than two at a time and trajectories of these atoms are evaluated by numerically solving Newton’s equations of motion for a many body system. It has been predicted by analytical theory [84] and found experimentally [85]
that different isotope of an element sputter preferentially. In this context it will be interesting to determine experimentally the angular distributions of $^{69}$Ga and $^{71}$Ga sputtered from the layer underneath the Bi monolayer.
APPENDIX A

FACTORS INFLUENCING THE ANGULAR SPUTTERING YIELD
Different misalignments in the collection geometry were possible in the sputtering set-up used for these studies. The effects of these asymmetries on the measured angular distributions of sputtered materials are apparent in Figs. 1.7 and 2.6. These misalignments were compensated for in the model used to fit the distribution mentioned in Chapter 1 and 2. Fig. A.1 illustrates the various possible offsets in the plane of the collection region. The collector can be translated with respect to the sputtered point on the target and rotated slightly with respect to the beam axis. We can relate the measured distribution to the anticipated form of the differential angular sputtering yield by designating offsets parallel to the target face by $r_C$, perpendicular to the target face by $r_F$ and rotations with respect to the beam axis by $D$. Thus assuming that the actual sputtering yield is of the form

$$ Y(\theta') = A \cos^B(\theta') $$

where $\theta'$ is the true polar angle with respect to the target normal, the corresponding differential sputtering yield is given as

$$ \frac{dY}{d\Omega}(\theta') = \frac{n(\theta) \cdot r'^2}{N_0} $$

\[\text{Figure A.1. Schematic of the collection geometry with possible offsets.}\]
where $n(\theta)$ and $N_0$ are the number density of atoms on the collector foil and number of incident projectiles during sputtering, respectively. Also, $\theta'$ and $r'$ in equations (59) and (60) are expressed in terms of $\theta$, $r$, $C$, and $D$ as

\begin{align}
(61) \quad r' &= r\sqrt{1 + C^2 + F^2 - 2[C \sin(\theta - D) + F \cos(\theta - D)]} \\
(62) \quad \theta' &= \arccos \frac{\cos(\theta - D)}{\sqrt{1 + C^2 - 2[C \sin(\theta - D) + F \cos(\theta - D)]}}
\end{align}

Hence, the corresponding differential sputtering yield in terms of $A$, $B$, $C$, $D$ and $\theta$ can be written as

\begin{align}
(63) \quad \frac{dY}{d\Omega} &= \frac{A \cos(\theta - D)^B}{[1 + C^2 + F^2 - 2[C \sin(\theta - D) + F \cos(\theta - D)]]^{\frac{B}{2} + 1}}
\end{align}

Eq. (63) was fitted to the measured distributions of sputtered particles to determine values of free parameters $A$, $B$, $C$, and $D$. $F$ was not zero in all cases, but could be measured in sputtering setup.
APPENDIX B

RUTHERFORD BACKSCATTERING SPECTROMETRY: THEORY
B.1. Introduction

Rutherford backscattering is a simple yet strong experiment, both conceptually and in its elementary execution. When a well collimated beam of mono-energetic particles impinges perpendicularly on a thick target, then the particles scattered backward by angles of more than $90^\circ$ from the incident direction can be detected. A particle detector is positioned at a desired angle to detect the backscattered particles reflected from the nuclei of the target atoms. The purpose of this chapter is to explain briefly the basics of Rutherford backscattering spectrometry (RBS). The concept of RBS is documented in detail in [86].

B.2. Kinematic Factor

Consider a projectile of mass $m_1$ and initial velocity $\vec{v}_0$, that undergoes an elastic collision with a particle of mass $m_2$ initially at rest. The conditions for treating the collisions as essentially elastic are that the projectile energy $E_0$ must be much greater than the binding energy of the atoms in the target and nuclear reactions and resonances must be absent. Fig. B.1 shows a schematic representation of an elastic collision between two masses. The principles of conservation of energy and momentum can be applied to solve the elastic collision between the projectile and target atom. After the collision, the projectile and the target atom have velocities and energies $v_1$, $v_2$, $E_1$, and $E_2$, respectively. The scattering angle $\vartheta$ and the recoil angle $\phi$ are defined as positive numbers and are also shown in the Fig. B.1.

Conservation of energy yields

$$
\frac{1}{2} M_1 v_0^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2.
$$

Conservation of momentum parallel to the direction of incidence yields

$$
M_1 v_0 = M_1 v_1 \cos \vartheta + M_2 v_2 \cos \phi.
$$

Conservation of momentum perpendicular to the direction of incidence yields

$$
0 = M_1 v_1 \sin \vartheta - M_2 v_2 \sin \phi.
$$
Eqs. (64) – (66) can be easily rearranged to find

\[
\frac{v_1}{v_0} = \left[ \frac{\pm (M_2^2 - M_1^2 \sin^2 \vartheta)^{1/2} + M_1 \cos \vartheta}{M_2 + M_1} \right].
\]

Finally, the kinematic factor \( K \), defined as the ratio of projectile energy after the collision to that before the collision follows from Eq. (67) as

\[
K = \left\{ \frac{\left[ 1 - (M_1/M_2)^2 \sin^2 \vartheta \right]^{1/2} + (M_1/M_2) \cos \vartheta}{1 + M_1/M_2} \right\}^2.
\]

B.3. Scattering Cross-section

The need for knowledge of the scattering cross section arises from a basic question: how frequently does a collision described in the previous section occur and ultimately result in a scattering event at a certain angle \( \vartheta \) ?

Fig. B.2 shows a beam of small width incident upon a thin uniform target. A detector of a known active area is placed at an angle \( \beta \) measured clockwise from beam axis in the figure. Hence the scattering angle is \( \vartheta = 180^\circ - \beta \). The particles are scattered into a differential solid angle \( d\Omega \).
Figure B.2. Representation of the scattering cross section.

The differential scattering cross-section is defined as

\[ \frac{d\sigma}{d\Omega} = \left( \frac{1}{Nt} \right) \left[ \frac{dQ}{d\Omega} \frac{d\Omega}{Q} \right], \]

where \( Q \) is the total number of particles impinging on the target, \( dQ \) is the number of particles recorded by the detector, and \( N \) is the volume density of atoms in the target with thickness \( t \).

Hence, the average differential scattering cross-section \( \sigma \) is obtained by integrating the differential scattering cross-section over a finite solid angle \( \Omega \), and yields

\[ \sigma = \left( \frac{1}{\Omega} \right) \int_{\Omega} \left( \frac{d\sigma}{d\Omega} \right) d\Omega. \]

The expression for the total number of detected particles \( A \) from Eqs. (69) and (70) is

\[ A = \sigma \Omega \cdot Q \cdot Nt. \]

The following assumptions can be made in calculating the differential cross-section for an elastic collision:

\[ \text{(68)} \]
• The force that acts during the collision between the projectile and target atom must be described by coulombic repulsion of the two nuclei.

• This will happen when the distance of closest approach is large compared to nuclear dimensions and small compared to the Bohr radius, $a_0 = 0.53 \, \text{Å}$. Rutherford’s formula for the differential scattering cross-section with respect to center-of-mass coordinates can be used when these assumptions are made [87, 88, 89]:

\[
\left( \frac{d\sigma}{d\Omega} \right)_c = \left[ \frac{Z_1 Z_2 e^2}{4 E_c \sin^2(\vartheta_c/2)} \right]^2
\]

where $Z_1, Z_2$ are the atomic numbers of the projectile and target atom, respectively, $e$ is the electronic charge and $E_c$ is the energy of the projectile before scattering.

The transformation of Eq. (72) from the center-of-mass frame to the laboratory frame of reference gives

\[
\frac{d\sigma}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4 E_c} \right)^2 \frac{4}{\sin^4 \vartheta} \left( \frac{1 - ((M_1/M_2) \sin \vartheta)^2)^{1/2} + \cos \vartheta \right)^2.
\]

Whenever the distance of closest approach is of the order of the Thomas-Fermi screening radius, [i.e., whenever the scattering event happens outside of or in the vicinity of the electron cloud] there will be deviations from Eq. (73) due to screening of the electrostatic potential of the target nucleus by its atomic electrons. When the incident particle penetrates the electron cloud around the target nucleus, it experiences a repulsive force. However, in a pure Rutherford scattering event, it is assumed that this repulsive force is always present. Lecuyer et al. [90] have calculated a correction factor due the screening of the electrostatic potential. They have considered a case where the distance of closest approach is smaller than the screening radius, but larger than the De Broglie wavelength.

Considering the above-mentioned approximations, Lecuyer et al. [90] obtained a screened cross-section:

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{screened}} = \left( \frac{d\sigma}{d\Omega} \right) \left( 1 - \frac{0.049 Z_1 Z_2^{4/3}}{E} \right).
\]

The correction factor $F$, where
\[ F = 1 - \frac{0.049 Z_1 Z_2^{4/3}}{E}, \]

is only dependent on the target atom and projectile atomic numbers and projectile energy before scattering. For a 2.0 MeV Si beam, the predicted deviation from Rutherford’s formula is \( \sim 12\% \).

### B.4. Energy Loss and Stopping Cross-section

When an energetic particle impinges on a very thin target of thickness \( \Delta x \), it slows down because of its interaction with the target nuclei (nuclear stopping) and target electrons (electronic stopping) and its energy \( E \) decreases. The amount of energy lost per distance traversed, \( \Delta E/\Delta x \), depends on the mass and the velocity of the projectile and on the composition and density of the target. In Fig. B.3, \( E_i \) is the energy of the incident particle, \( E_x \) is the energy before a scattering event at a depth \( x \), and the energy of the particle emerging from the surface is \( E_f \). The scattering angle in the laboratory frame is given by \( \vartheta = 180^\circ - \vartheta_1 - \vartheta_2 \), where \( \vartheta_1 \) and \( \vartheta_2 \) are the angles between the normal and the direction of the incident beam and the direction of the scattered particle, respectively. We can relate the energy \( E_x \) to the length \( x/\cos \vartheta_1 \) of the incident path by

\[
(76) \quad \frac{x}{\cos \vartheta_1} = -\int_{E_i}^{E_x} \frac{dE}{(dE/dx)}
\]

Similarly we can relate the energy \( KE_x \) to the length \( x/\cos \vartheta_2 \) of the outward path by

\[
(77) \quad \frac{x}{\cos \vartheta_2} = -\int_{KE_x}^{E_f} \frac{dE}{(dE/dx)}
\]

If we assume a constant value for \( dE/dx \) along the inward and the outward paths, then Eqs. (76) and (77) reduce to

\[
(78) \quad E_x = E_i - \frac{x}{\cos \vartheta_1} \frac{dE}{dx} \bigg|_{\text{inward}}
\]

and

\[
(79) \quad E_f = KE_x - \frac{x}{\cos \vartheta_2} \frac{dE}{dx} \bigg|_{\text{outward}}
\]
The last two equations can be rearranged to give:

\[ \Delta E = KE_i - E_f = [S]x = \left[ \frac{K}{\cos \vartheta_1} \left| \frac{dE}{dx} \right|_{\text{inward}} + \frac{1}{\cos \vartheta_2} \left| \frac{dE}{dx} \right|_{\text{outward}} \right] x. \]

where \( KE_i \) is the energy of the particles scattered from atoms at the surface of the target, \( \Delta E \) is the symbol for the energy difference between \( KE_i \) and \( E_f \), and \([S]\) is called the energy loss factor (commonly known as the \( S \) factor). Generally, the stopping cross-section factor \( \varepsilon \), defined as

\[ [\varepsilon] = \frac{[S]}{N}, \]

is used rather than \( dE/dx \). Hence, Eq. (80) becomes

\[ \Delta E = [\varepsilon]Nx, \]

where

\[ [\varepsilon] = \left[ \frac{K}{\cos \vartheta_1} \varepsilon_{\text{inward}} + \frac{1}{\cos \vartheta_2} \varepsilon_{\text{outward}} \right]. \]
B.5. Surface Energy Approximation

If the relative change in the energy of the incident ions is negligible for the regions near the surface, then \( (dE/dx)_{\text{inward}} \) and \( (dE/dx)_{\text{outward}} \) can be evaluated at \( E_i \) and \( KE_i \), respectively. This approximation is widely used in calculating the total number of counts expected in the backscattering signal and is called the surface energy approximation. Thus, under this approximation Eq.(83) takes the form

\[
\varepsilon_i = \left[ \frac{K}{\cos \vartheta_1} \varepsilon(E_i) + \frac{1}{\cos \vartheta_2} \varepsilon(KE_i) \right],
\]

where \( \varepsilon(E_i) \) and \( \varepsilon(KE_i) \) are evaluated at energies \( E_i \) and \( KE_i \), respectively.

B.6. Thin films

A thin film deposited on a substrate of atomic mass lighter than the element in the film and containing \( N_t \) atoms of a single element per unit area in the film is considered. The two quantities in the RBS signal that are directly related to the number of atoms per unit area contained in the film are the energy width \( \Delta E \) of the signal and the total number of the counts, \( A \).

The total number of counts is a quantity that one can easily extract from the backscattering spectrum by summing over all channels \( j \) in the spectral peak associated with the element:

\[
A \equiv \sum_j H_j.
\]

Here the spectrum height \( H_j \) in channel \( j \) is given as

\[
H_j = \frac{\sigma(E_j) \Omega Q N \tau_j}{\cos \vartheta_1}
\]

where \( \sigma(E_j) \) is the average differential scattering cross section between the projectile and the sample evaluated at energy \( E_j \), \( \Omega \) is the solid angle spanned by the detector active area, \( Q \) is the total number of incident projectiles bombarding the sample, and \( N \tau_j \) is the number of atoms per unit area in a region of thickness \( \tau_j \) corresponding to the channel \( j \) at depth.
$x_j$. $E_j$ is the difference between the initial energy $E_i$ and the energy that the particle loses along the incident path and is given by

$$E_j = E_i - \left( N x_j / \cos \vartheta_1 \right) \varepsilon(E).$$

In the limit of continuous variables $x$ and $E$ and for a film of thickness $t$, the expression for $A$ takes the form:

$$A = \left( Q \Omega N / \cos \theta_1 \right) \int_0^t \sigma(E) dx.$$

If the surface energy approximation is applied in determining the total number of counts, which means the energy lost by an incident particle on traversing a thin film is negligible compared to its initial energy $E_i$, i.e., the variable $E$ equals $E_i$ throughout the film, then the total number of counts becomes

$$A = \sigma(E_i) \Omega Q N t / \cos \theta_1.$$

Hence, under the surface energy approximation and for a normally incident beam the number of atoms per unit area takes the form

$$N t = \frac{A}{\sigma(E_i) Q \Omega}.$$

B.7. Conclusions

It can be concluded that the thickness of the unknown sample can be determined with high precision using back scattering spectrometry under the condition that the target is thin so that the energy loss of the incident beam is negligible. Such condition were found to hold for the collector foils analyzed in this study.
APPENDIX C

RUTHERFORD BACKSCATTERING SPECTROMETRY: EXPERIMENT
C.1. Introduction

Rutherford backscattering spectroscopy (RBS) has been extensively used for a number of years as an important tool for materials analysis. As an extension of this technique, Heavy Ion Rutherford backscattering spectroscopy (HIRBS) has gained importance in the last few decades as a surface analysis technique due to its improved mass and depth resolution, and sensitivity as compared to conventional RBS [91, 92]. For absolute determination of elemental distributions, both techniques require accurate charge measurement to determine the number of ions incident on a target under varied conditions of sample and scattering geometry. When fast ions impinge upon a solid target, they produce secondary electrons that can carry charge away from the target. These secondary electrons and particle-induced photons may in turn produce tertiary electrons when they encounter the first solid surface, which can carry charge back to the target. In addition to this, the incident primary ion beam may be accompanied by incident electrons which originate at collimators, slits or other electron sources [93]. Hence these complications make accurate current integration a consequential task. Measurements similar to those described here have been reported for light ions where accuracy of current measurements using a Faraday cup was questioned [38]. When energetic heavy ions such as oxygen impinge on a target, the number of secondary electrons generated is significantly higher than for light ions, and can exceed the number of incident ions by orders of magnitude, so suppression of secondary and tertiary currents is all the more critical. To complete the picture, knowledge of the absolute beam energy and energy spread is critical for many measurements in ion beam analysis and hence creates a need for accelerator energy calibration [94]. In the present work we were able to suppress all the incident electrons originating at the slits or collimator by introducing an electron trap in the beam path. In addition to this, the target was surrounded by a biased mesh to suppress secondary electrons and minimize the production of tertiary electrons.

C.2. Experiment

Fig. C.1 shows the overall layout of the accelerator system used in this study. To test the target current integration system, oxygen (O) ions produced by a National Electrostatics
Corporations (NEC) source of negative ions by cesium sputtering (SNICS II) were used. For this experiment ZnO was used as a cathode material to produce $\text{O}^-$ ions. 30 keV energetic $\text{O}^-$ ions were injected into a 3 MV NEC 9SDH-2 Pelletron accelerator with terminal voltage set at 1.0 MV and 1.5 MV as measured by a generating voltmeter (GVM), the readout for which is reproducible and stable over days at the 0.05% level. An analyzing magnet was used to deflect doubly charged ions, $\text{O}^{2+}$, into the target chamber beamline. After acceleration and analysis, the ion beam was focused using an electrostatic quadrupole doublet lens to a spot size of $\sim 1 \text{ mm} \times 2 \text{ mm}$ on the target. The vacuum was well maintained at the various stages of the beam line, ranging from $\sim 5 \times 10^{-8}$ Torr to $1 \times 10^{-9}$ Torr. Fig. C.1 shows a layout of the ion source, Pelletron accelerator, analyzing magnets and beamline used for this
Figure C.2. Photograph of the RBS setup for target thickness analysis: A) biased wire mesh surrounding the target holder, to suppress secondary electrons; B) top of target holder - a target mounted on the holder can be seen behind the wire mesh screen; C) solid state surface barrier detector; and D) electron trap to suppress electrons generated in beam path.
Fig. C.2 shows a photograph of the interior of the multi-purpose chamber attached to the end of one of the four beam-lines for the 3 MV accelerator. Fig. C.3 shows a schematic of the biasing arrangement and data acquisition system. During measurements the electron trap and mesh were biased at voltages ranging from 0 V to $-700$ V. The target holder could also be moved out of the way to measure the beam current in a downstream Faraday cup. The targets used for this experiment were thin films of rhodium (Rh) on vitreous carbon (VC) and palladium (Pd) on VC. Detector active area was determined in a separate vacuum chamber by counting alpha particles from an $^{241}$Am source both with and without a collimator of known area in front of the detector. Two different solid state surface barrier detectors were used for these measurements, with active areas of 44.1 mm$^2$ (Det. 1) and 52.3 mm$^2$ (Det. 2), respectively. An Ortec model 142 pre-amplifier and 572 spectroscopy amplifier were used for data acquisition. Accuracy of the charge integrator used in this experiment was checked with a current source and was found to be better than 1%. Beam currents ranging from $\sim 1$ nA to $\sim 5$ nA of O$^{2+}$ were used for HIRBS and an integrated charge on the target of $\sim 1$ µC was accumulated for each measurement. Measurements were made
on several different days, with slight variations in detector position; the nominal scattering angle was $153^\circ$, and the detector distance from the target was $\sim8$ cm.

C.3. Results

Fig. C.4 shows a representative oxygen backscattering spectrum obtained from the rhodium on VC target. The spectra for the Pd target were very similar. Note that there are no backscattered oxygen ions from the less massive carbon atoms in the substrate. The only feature in the spectrum is the single peak from the thin film of Rh atoms. The breadth and apparent low energy of the backscattered peak are attributed to the pulse height defect for the heavy oxygen ions in the solid state detector. The area under the backscattered peak, corrected for dead time, along with the integrated beam charge, detector solid angle, and calculated Rutherford scattering cross section, was used to calculate an areal density for the target material. The Rutherford scattering cross-section was modified to take into account the electronic screening of the nucleus [90].
Figure C.5. Plot of apparent areal density of Rh on VC vs. bias voltage under varying experimental conditions: A) and B) 3.0 MeV O\textsuperscript{2+} with no electron trap, respectively; C) 3.0 MeV O\textsuperscript{2+} with electron trap; D) through G) 4.5 MeV O\textsuperscript{2+} with electron trap. F) and G) were made with low and high beam current, respectively. Det. 2 was used for series A and Det. 1 was used for series B through G.

The areal density calculated in this manner is plotted in Figs. C.5 and C.6 for the Rh and Pd targets, respectively, as a function of the applied bias voltage under a variety of experimental conditions. Note that the maximum kinetic energy an electron can acquire in an elastic collision with an oxygen ion is $T_{\text{max}} = 4(m_e/m_i)E$, where $E$ is the incident ion energy, and $m_i$ and $m_e$ are the ion and electron masses, respectively. For a 4.5 MeV O\textsuperscript{2+} ion, the maximum energy transferred to an electron will thus be approximately 600 eV. Hence, it is anticipated that all primary and secondary electrons should be suppressed by bias voltages of $-700$ V. We applied biases ranging from 0 V up to $-700$ V or $-800$ V to study the effect...
Figure C.6. Plot of apparent areal density of Pd on VC vs. bias voltage under varying experimental conditions: A) and B) 3.0 MeV O\(^{2+}\) with no electron trap; C) 3.0 MeV O\(^{2+}\) with electron trap; D) 4.5 MeV O\(^{2+}\) with electron trap. Det. 2 was used for series B and Det. 1 was used for series A, C and D.

of the primary and secondary electron currents on calculated areal density.

In Fig. C.5, a large change in the apparent areal density as a function of applied bias is clearly evident. At zero bias, the large secondary electron current from the target causes the measured current to be much larger than the actual ion current, which results in an undercounting of backscattered ions and a low calculated target areal density. As the bias is increased, the electron currents are suppressed, and the calculated areal density increases. The value of the areal density is observed to stop changing above \(-700\) V bias for the 4.5 MeV ion beam, as anticipated. In Fig. C.5, series D through F were all measured using 4.5 MeV ions with the trap, on different days, and the scatter in measured values at \(-700\) V bias.

81
and above is within $\sim 1\%$ of the mean. Series F and G were measured using beam currents $\sim 50\%$ higher and $\sim 50\%$ lower, respectively, than were used for the other series. Series A through C in this figure were measured using 3.0 MeV ions. Series A and B were measured using different detectors (and show no meaningful difference), but without the electron trap. Hence the difference between these and series C may be attributed to electrons traveling with the beam. Series C saturates at an areal density that is $\sim 4\%$ higher than that for the 4.5 MeV measurements; we suspect this is likely due to uncertainty in the energy calibration of our GVM.

Fig. C.6 shows similar results for measurements on the Pd target. Here again, series A and B were measured using different detectors with 3.0 MeV ions without the electron trap, and series C was measured at the same energy with the trap. Series C shows smaller areal densities than A and B, which we again attribute to the suppression of electrons traveling with the beam. Series D was measured using 4.5 MeV ions with the trap, and at 700 V shows an areal density $\sim 3\%$ below that for series C, similar to that observed for the corresponding series in Fig. C.5. Statistical uncertainties for all but the zero bias points plotted in Figs. C.5 and C.6 were $\sim 0.5\%$. Detector solid angles were measured with $\sim 2\%$ uncertainty, and backscattering angles with $\sim 0.2^\circ$ uncertainty.

C.4. Conclusions

By applying increasing bias voltages during HIRBS measurements, we have observed measured values for corresponding target areal densities to stabilize at biases consistent with suppressing all primary and secondary electron currents on the target. Using 4.5 MeV oxygen projectile ions, we found measured areal densities to be reproducible to within $\pm 1\%$ on a day-to-day basis. Measurements made using 3.0 MeV ions were $\sim 3\%$ higher, but this may be due to energy calibration rather than current integration errors.
BIBLIOGRAPHY


83


[33] A. Sommerfeld, Zeitschrift für Physik 78 (5-6) (1932) 283–308. 14


85


[87] E. Rutherford, Phil. Mag. 21 (1911) 669. 69