AN INVESTIGATION OF SPUTTERING AND SECONDARY ION EMISSION FROM POLYCRYSTALLINE METAL FOILS UNDER MEV HEAVY ION BOMBARDMENT

JOHN PATRICK O'CONNOR

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In these experiments, sputtering and secondary ion emission from metals have been studied during MeV heavy ion bombardment. One purpose of the measurements was to determine if the ejection of the sputtered particles was consistent with a collisional description of the sputtering process. Another purpose was to determine if the large electronic excitation of the sample during the high energy irradiations would result in patterns of secondary ion emission that were significantly different from those observed during keV ion bombardments. During the investigation, three analytical techniques were used: secondary ion mass spectrometry, secondary ion energy spectrometry, and total sputtering yield measurements.

The mass spectrometric measurements consisted, in part, of a comparison of positive secondary ion emission during 100 keV ⁴⁰Ar⁺ and 70 MeV ⁷⁹Br⁺ ion bombardment of several targets. The results of these measurements demonstrated that the MeV projectiles were substantially more efficient in producing positive secondary ions of electronegative surface constituents. To supplement these observations, the variation of ion emission from Al, V, and Y surfaces was measured as a function of ⁷⁹Br projectile energy. In these measurements, it was observed that the emission of Al⁺ and V⁺ secondary ions was roughly proportional to the nuclear stopping cross section for Br in the targets. In contrast, the yields of positive ions of electronegative surface constituents increased significantly as the Br energy increased from 100 keV to about 20 MeV. Above this energy, the yields of the electronegative species were approximately
independent of energy. During the measurements of secondary ion mass spectra, additional information regarding the energies of the ions was obtained. This information indicated that the energies of the non-metallic secondary ions were at most 20 eV.

Measurements of integrated secondary ion energy spectra were obtained from Cu, Nb, and Ta foils during 75 MeV $^{79}$Br$^{8+}$ ion bombardment. The energy distributions were observed to peak at about 2 eV. However, the decrease above the most probable energy was much more rapid than for atomic ions sputtered by keV projectiles. In fact, essentially all ions that we observed had energies below 20 eV. This result is consistent with the conclusion that the energy spectra are dominated by non-metallic secondary ions.

Total sputtering yields were obtained from Nb and Y targets during 70 MeV $^{79}$Br$^{7+}$, 100 keV $^{40}$Ar$^+$, and 100 keV $^{79}$Br$^+$ bombardment. The yields for the 70 MeV projectiles were 0.14±0.03 and 0.14±0.04 for Nb and Y, respectively. In both cases, the measured yields are consistent with the predictions of collision cascade theory.

This consistency indicates that collisional sputtering is the dominant mechanism for the sputtering of metals during high energy projectile bombardments. The observations that the yields of Al$^+$ and V$^+$ are proportional to the nuclear stopping cross sections indicate that these ions were also produced as a result of a collision cascade. The fact that the positive ions of electronegative species increase with projectile energy and that these ions have very low energies clearly demonstrates that they are not collisionally produced. None of the models that we have considered, however, are capable of fully explaining the trends in the emission of these secondary ions.
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A Dissertation
Presented to the Faculty of the Graduate School of Yale University
in Candidacy for the Degree of Doctor of Philosophy

John Patrick O'Connor
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To Cindy
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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION AND THEORETICAL BACKGROUND</td>
<td>1</td>
</tr>
<tr>
<td>1.1 General Introduction and Motivation</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Scope and Organization</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Sputtering of Metals</td>
<td>3</td>
</tr>
<tr>
<td>1.3.1 Collisional Sputtering</td>
<td>3</td>
</tr>
<tr>
<td>1.3.2 Semi-Empirical Formula of Matsunami et al. (Ma84)</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Models of Secondary Ion Emission for Low Energy Ion Bombardment</td>
<td>7</td>
</tr>
<tr>
<td>1.4.1 Thermodynamic Models</td>
<td>8</td>
</tr>
<tr>
<td>1.4.2 Chemical Models</td>
<td>11</td>
</tr>
<tr>
<td>1.4.3 Quantum Mechanical Models</td>
<td>13</td>
</tr>
<tr>
<td>CHAPTER 2 SECONDARY ION MASS SPECTROMETRY</td>
<td>24</td>
</tr>
<tr>
<td>2.1 General Description of Measurements</td>
<td>24</td>
</tr>
<tr>
<td>2.2 Accelerators, Vacuum Hardware, and Targets</td>
<td>25</td>
</tr>
<tr>
<td>2.3 Quadrupole Mass Spectrometry</td>
<td>27</td>
</tr>
<tr>
<td>2.4 Quadrupole Mass Filter</td>
<td>28</td>
</tr>
<tr>
<td>2.5 Ion Energy Selection by Voltage Modulation</td>
<td>29</td>
</tr>
<tr>
<td>2.5.1 General Technique</td>
<td>29</td>
</tr>
<tr>
<td>2.5.2 Data Acquisition</td>
<td>30</td>
</tr>
<tr>
<td>2.5.3 Measurements and Results</td>
<td>32</td>
</tr>
<tr>
<td>2.5.3.1 Preliminary Measurements</td>
<td>32</td>
</tr>
</tbody>
</table>
2.5.3.2 Comparison of Secondary Ion Emission During
70 MeV $^{79}$Br$^{7+}$ and 100 keV $^{40}$Ar$^{+}$ Bombardment.............. 34

2.5.3.3 Analysis of Uncertainties................................................... 39

2.5.3.4 Variation of Ion Yields as a Function of Projectile Energy...... 42

2.6 Energy Selection by a Commercial Electrostatic Energy Analyzer............... 45

2.6.1 Instrument and Procedure........................................................... 45

2.6.2 Measurements........................................................................... 46

2.6.3 Results...................................................................................... 47

CHAPTER 3 SECONDARY ION ENERGY SPECTROMETRY......................... 81

3.1 The Spectrometer................................................................................. 82

3.2 Operation............................................................................................. 83

3.3 Data Acquisition................................................................................... 84

3.4 Analysis of the Spectrometer................................................................. 85

3.4.1 Theoretical Analysis................................................................... 85

3.4.2 Experimental Calibration............................................................. 86

3.5 Measurements and Results................................................................. 87

3.6 Analysis of Uncertainties................................................................... 90

CHAPTER 4 TOTAL SPUTTERING YIELD MEASUREMENTS...................... 102

4.1 Collection of Sputtered Material............................................................. 102

4.2 Analysis of Collected Material............................................................... 104

4.2.1 Heavy Ion Rutherford Backscattering........................................... 105

4.2.2 Alpha-Particle Rutherford Backscattering..................................... 106

4.2.3 Testing of the Backscattering Apparatus...................................... 107

4.3 Data Analysis....................................................................................... 107

4.4 Results................................................................................................. 109
INTRODUCTION AND THEORETICAL BACKGROUND

CHAPTER 1

1.1 General Introduction and Motivation

The impact of an energetic atom or ion with the surface of a solid may result in the emission of atoms, clusters of atoms, ions, or electrons from the material. This process, known as sputtering, was first observed more than one hundred years ago in gas discharges when cathode material was deposited on the surrounding glass walls (Gr53, Ga58, Pl58). The presence of secondary ions among sputtered atoms was first noted by Thompson approximately fifty years later (Th10). Today, sputtering and secondary ion emission are known to be ubiquitous effects of ion beam irradiation of materials, present at some level for almost any projectile-target combination for virtually any projectile energy above a few eV.

These processes have been studied extensively using low energy projectiles. A large body of information now exists concerning sputtering of elemental metallic targets by beams with energies below about 1 MeV (An81, Ma84, and references therein). Similarly, many studies of secondary ion emission from metals bombarded by projectiles with energies below 100 keV have been performed (Bi79, Wi77b, Wi79a, Wi82a, and references therein). In contrast, measurements using high energy primary ions are scarce. Therefore, the experiments described in this dissertation were designed to investigate sputtering and secondary ion emission from metallic targets bombarded by MeV heavy ions.

The paucity of data for high-energy projectiles was the principal, but not sole, reason for performing these measurements. A number of additional observations indicated that new insights into the sputtering or secondary ion formation mechanisms could be obtained by studying metals irradiated by MeV heavy ions. The first set of observations concerned sputtering yields, which are defined as the mean number of sputtered particles per incident ion. For primary ions below 1 MeV,
the accepted theory of sputtering (Si69, Si72) (Section 1.3) predicted that yields were proportional to the nuclear stopping power of the target. This prediction was in reasonable agreement with the bulk of the data obtained from metallic targets bombarded by low energy projectiles. However, a number of workers have recently observed that the sputtering yields of many dielectric materials bombarded by MeV primary ions were two to three orders of magnitude greater than the yields predicted by theory. Moreover, the yields were related to the energy deposited by the projectile in electronic excitations of the target (Jo82 and references therein). Since the effects of the electronic energy loss on metallic sputtering have not been studied in detail (Ba76b, Gr79, Ni76), the results for dielectric targets indicate that these effects should be further investigated.

The second set of observations concerned desorption and ionization of large biomolecules. In 1974, Macfarlane and co-workers demonstrated that $^{252}$Cf fission fragments were capable of desorbing and ionizing large biomolecules intact (To74, Ma76). Subsequently, Benninghoven et al. showed that similar results could be obtained with keV projectiles (Be76, Be83b). As a result of these measurements, the mechanisms of biomolecule desorption and the role of the projectile energy have been a matter of dispute. In addition, their work highlights the fundamental question of whether one should expect to observe qualitative changes in secondary ion emission as a result of increasing the projectile energy from a few keV to tens of MeV. This question may be answered more directly by the use of relatively simple metallic targets with few contaminants instead of studying the desorption and ionization of complex biomolecules.

1.2 Scope and Organization

Three analytical approaches were used during our studies of sputtering and secondary ion emission: secondary ion mass spectrometry, secondary ion energy spectrometry, and total sputtering yield measurements. Secondary ion mass spectra should provide the most distinct signatures of qualitative changes in secondary ion emission for projectiles with keV and MeV
energies. Also, measurements of the variation of secondary ion yields of individual species by mass spectrometry as a function of primary ion energy may indicate which mechanisms for secondary ion emission are dominant at high projectile energies. Measurements of secondary ion energy spectra have been performed because of the considerable value of neutral atom energy spectra in distinguishing between sputtering mechanisms (Gr80, We78). Although secondary ion energy spectra are more difficult to interpret because of the uncertainty of the ionization mechanisms (Section 1.4), they provide complementary information to the secondary ion mass spectra. Also, significant differences in energy spectra obtained with keV and MeV projectiles would suggest that different physical processes (of ionization or sputtering or both) were dominant in each case. Total sputtering yield measurements have been performed because the collision cascade theory of metallic sputtering (Section 1.3) makes specific predictions for yields obtained during MeV projectile bombardment. Significant deviations from these predictions, as observed for dielectric materials (Jo82 and references therein), would indicate that electronic energy loss processes were also important in the sputtering of metals by high energy primary ions.

In the remaining sections of this chapter, the theoretical description of metallic sputtering, the general features of secondary ion emission, and models of secondary ion formation for keV projectiles are presented. The measurements that we have performed are presented in Chapters 2-4. A discussion of the results with respect to the theories presented below, as well as conclusions and possible future directions, are presented in Chapter 5.

1.3 Sputtering of Metals
1.3.1 Collisional Sputtering

The sputtering of metals by low energy projectiles is recognized to be the result of elastic collisions of the incident ion with target atoms but the process proceeds by three qualitatively different mechanisms (Si81). In the single knock-on regime (Figure 1.1a), which occurs for
projectile energies near the threshold for sputtering, target atoms may be ejected directly by the projectile or after a small number of collisions. More often, the impact of an energetic ion will generate a linear collision cascade (Figure 1.1b). In this situation, the projectile collides with a small number of target atoms. (Only elastic collisions are expected to produce appreciable atomic motion because the relaxation time of the conduction electrons is short enough (approximately $10^{-14}$ s) that even if the projectile lost a significant amount of energy through ionization and excitation of electrons, the energy would be immediately shared among all the conduction electrons in the solid (Si81).) The struck atoms, called primary recoils, are displaced from their lattice sites and transfer energy to nearby atoms through elastic or quasi-elastic collisions. These secondary recoils collide with additional atoms and the process evolves through many generations. In a short time (approximately $10^{-13}$ s), the energy lost by the incident ion in elastic collisions has been shared among a large number of atoms which are distributed isotropically around the path of the projectile in a collision cascade. Some of these atoms may be directed out of the target surface and will escape if they have sufficient energy to overcome the surface binding energy of the solid.

The radius and lifetime of the cascade, and therefore the number of sputtered atoms, are determined by the energy lost by the projectile per unit path length in the target. Since only elastic ion-target collisions are expected to produce atomic motion, the yield of sputtered atoms is determined by the nuclear stopping component of the stopping power. By considering a cascade where the density of recoiling atoms was sufficiently low so that collisions between moving atoms were infrequent, Sigmund quantified this relationship using the linearized Boltzmann transport equation (Si69, Si72):

$$S(E)=0.042 \alpha S_N(E) \sec \Psi/U_0 \quad (1/\Lambda^2) \quad (1.1)$$

where $\alpha$ is a dimensionless function of the angle of incidence, the projectile-target mass ratio, and
the projectile energy $E$: $S_N(E)$ is the nuclear stopping cross section (Li68); $\Psi$ is the angle of the beam with respect to the target normal; and $U_0$ is the surface binding energy (commonly approximated by the sublimation energy). Values of $\alpha$ for keV projectiles have been determined by Winterbon (Wi75a). For projectile energies in the Rutherford scattering regime, $\alpha$ is predicted to be 1/2 (Si69) if only elastic interactions are considered. The nuclear stopping cross section may be determined using the empirical formulae developed by Winterbon et al. (Wi70).

In addition, for perpendicularly incident ions, the linear cascade theory predicts that the sputtered particles will be emitted in a cosine distribution around the target normal. This angular distribution is a consequence of the isotropic flux of atoms inside the target (Si81). However, surface roughness and crystallinity, as well as anisotropic components of the cascade, will cause deviations from a simple cosine distribution for the sputtered flux. These deviations have often been observed for targets bombarded by keV projectiles (An85 and references therein). Finally, the energy distributions of sputtered atoms are predicted to peak at low energies (at approximately 1/2 of the binding energy) and to decrease asymptotically as approximately $1/E^2$. This energy dependence of the sputtered atoms has been observed during keV projectile bombardment of Au and U by Thompson (Th68) and Weller (We78), respectively.

The third mechanism for metallic sputtering occurs when the density of recoil atoms in a cascade is so high that the majority of atoms within a certain volume are in motion (Figure 1.1c). This situation is termed a spike (Si81). Sputtering from spikes may be non-linear and the non-linear Boltzmann equation must be used to describe the physical situation. Spike phenomena have been observed in comparisons of atomic ion and diatomic molecular ion bombardments (An74, An75b) and also in sputtering of heavy targets by heavy projectiles (Ba76b, Th81).
1.3.2 Semi-Empirical Formula of Matsunami et al. (Ma84)

Although the sputtering yields that are predicted by eq. (1.1) are in reasonable agreement with data obtained from a variety of targets bombarded by projectiles with energies up to about 1 MeV, systematic deviations from predicted values have been observed for light-ion sputtering (Be70b) and low-energy heavy ion sputtering (Si81). For light ions, primary ions that are backscattered from the interior of the solid have been shown to account for a significant fraction of the processes leading to sputtering (Be70b). For heavy ion sputtering near threshold, i.e. the single knock-on regime, recoil atoms do not undergo a sufficient number of collisions prior to ejection to lose memory of the projectile. As a result, the velocity distribution of recoil atoms is not isotropic as assumed in the derivation of eq. (1.1) (Si69, Si81). To include these effects, Matsunami et al. (Ma84) proposed the following semi-empirical formula for sputtering of a target of atomic number \( Z_2 \) and atomic mass \( A_2 \) by a projectile of atomic number \( Z_1 \) and atomic mass \( A_1 \):

\[
S(E) = 0.42 \alpha^* Q K s_n(\epsilon)(1-(E_{th}/E)^{0.5})^2/(U_s(1+0.35U_s s_e(\epsilon)))
\]

where \( S(E) \) is the sputtering yield for projectiles of energy \( E \); \( U_s \) is the sublimation energy; \( \alpha^* \), \( Q \), and \( E_{th} \) are empirical parameters which were obtained from a best fit to the data subject to certain restrictions; and, \( s_n(\epsilon) \) and \( s_e(\epsilon) \) are Lindhard's elastic and inelastic stopping cross sections, respectively (Li61, Li63). The reduced energy \( \epsilon \) is defined as:

\[
\epsilon = a_2 E/(Z_1 Z_2 e^2(A_1+A_2))
\]
where \( a = 0.885 a_0 (Z_1^{2/3} + Z_2^{2/3})^{1/2} \) and \( a_0 \) is the Bohr radius. The parameter \( K \) is the conversion factor from the elastic reduced stopping cross section \( s_n(\varepsilon) \) to the stopping cross section in units of eV/(10^{15} \text{ atoms/cm}^2). The authors estimate that the yields predicted by eq. (1.2) are accurate to within \( \pm 20\% \) near the maximum of the sputtering yield curve and deviate somewhat more at lower and higher projectile energies. It is interesting to note that for high projectile energies, the expression for \( S_N(E) \) in eq. (1.1) varies as \( \ln(\varepsilon)/\varepsilon \), i.e. Rutherford with a slight asymptotic difference, while eq. (1.2) varies as \( \ln(\varepsilon)/\varepsilon^{1.5} \). For this reason, the predictions of eq. (1.2) are not suitable for comparison with measurements of total sputtering yields for projectiles in the Rutherford scattering regime.

1.4 Models of Secondary Ion Emission for Low Energy Ion Bombardment

Despite the many studies of secondary ion emission from metallic target surfaces that have been performed during the last two decades (Bl79, Wi77b, Wi79a, Wi82a and references therein), the complexity of the ion emission process has thus far precluded the development of a comprehensive theory of secondary ion formation. There are, however, a large number of models each of which is capable of rationalizing some components of secondary ion data. The most reproducible of these secondary ion phenomena are enumerated below (Wi79a):

**Observation #1.** Positive ion yields of different elements sputtered from a common matrix exhibit an inverse exponential dependence on the ionization potential of the emitted atom (An72, An75a). Negative ion yields appear to have an exponential dependence on the electron affinity of the sputtered atom (An75a).

**Observation #2.** The presence of oxygen or other electronegative elements at the target surface significantly enhances the yield of positive atomic metallic secondary ions (Bl79, Si66). Similarly,
the yield of negative secondary ions is increased by the presence of cesium or other electropositive species at the surface (Be77, Kr62). In addition, oxygen has been observed to increase negative ion yields (Mo73, Wi78).

Observation #3. Secondary ion energy distributions are generally observed to peak at low energies (5-10 eV) but they have slowly decreasing high energy tails which may extend up to hundreds of eV (Bl79 and references therein).

These observations form the basis for models that attempt to describe secondary ion emission during low-energy ion bombardment. A number of the proposed models which may be classified as thermal, chemical, or quantum mechanical are discussed below. In general, the models proceed from the assumption that the production of secondary ions is mediated by a collision cascade (Bl79, Ga83). Since the memory of the initiating collision is rapidly lost during the development of the cascade, atomic excitation and ionization are expected to be controlled by the properties of the surface atoms and to be insensitive to the nature of the primary ion (Wi79a). It is noted that not all the ion formation models are presented, but only those which include predictions which may be tested using MeV projectile bombardment. For a more comprehensive treatment, the reader is referred to several review articles (Bl79, Wi77b, Wi79a, Wi82a).

1.4.1 Thermodynamic Models

Thermodynamic models of secondary ion formation have been developed by Andersen and Hinthorne (An73, An75a), by Jurela (Ju73), and by Williams (Wi79a). In the model of Andersen and Hinthorne, secondary ions were postulated to be emitted from a sputtering region that resembles a dense plasma at local thermodynamic equilibrium (LTE). The ionization process is considered to be an equilibrium dissociation reaction such as:

\[ M^0 \rightarrow M^+ + e^- \quad \text{or} \quad M^0 + e^- \rightarrow M^+ \]
where $M$ = metal atom. The equilibrium concentrations of sputtered atoms, ions, molecules, and electrons may be predicted through the use of the appropriate Saha thermodynamic equations (Sa19, Sa20, Sa21). The yields of positive and negative secondary ions sputtered from a common matrix are predicted to have the form:

$$\frac{N^+}{N_0} \propto \exp\left(-\frac{I}{kT}\right) \quad (1.4)$$

$$\frac{N^-}{N_0} \propto \exp\left(\frac{E_a}{kT}\right) \quad (1.5)$$

where $N$ represents the sputtered object of interest; $I$ and $E_a$ are the ionization potential and electron affinity of the sputtered atom, respectively; $k$ is Boltzmann's constant; and $T$ is a fitting parameter (typically $10^4$ °K).

The dependence of the positive and negative ion yields on $I$ and $E_a$ predicted by eqs. (1.4) and (1.5) is in agreement with observations obtained with keV projectiles (observation #1 above), but the existence of a plasma at thermal equilibrium at the sputtering site has been severely questioned (Wi79a). In addition, measured secondary ion energy distributions are not Maxwellian (Bi79) and differ for different species sputtered from a common matrix (Kr77); ionization temperatures ($T$) differ for low and high energy secondary ions (Mo76); and, the predictions of eqs. (1.3) and (1.4) are correlated with the composition of the bulk of the material which may not correspond to the composition of the surface.

A model similar to that of Andersen and Hinthorne but developed from non-equilibrium thermodynamics has been proposed by Jurela (Ju73). In this case, the degree of ionization of positive ions, $R^+$, has the form:

$$R^+ \propto \exp\left[e(\phi - I(x_c)/kT\right] \quad (1.6)$$

where $\phi$ is the work function of the surface, $I(x_c)$ is the ionization potential of the sputtered particle at a critical distance for charge exchange (approximately one-half of the lattice constant), and $T$ is a
fitting parameter (~2000 - 5000 °K). Jurela speculated that the lower values for the temperature were more realistic than the results of Andersen and Hinthorne.

Williams (Wi79a) has also developed a thermal secondary ion emission model which is more realistic than that of Andersen and Hinthorne. In this surface electron excitation model, the sputtered particle is assumed to leave the surface at the same state of excitation as the sputtering site. Since the region of sputtering is highly excited, the particle is initially ionized. As it moves away from the surface up to a critical distance, the particle interacts electronically with the surface through resonant exchange processes. At that critical distance, the probability that the sputtered atom has an electron in a given energy level I is assumed to be equal to the probability $P_f$ that the corresponding energy level in the solid is occupied (Figure 1.2). Thus, the neutral flux of sputtered atoms is:

$$N_o = NP_f$$

where $N$ is the total flux of sputtered particles. Similarly, the flux of ions is determined by the probability $P_e$ that the given level, $I$, in the surface is vacant,

$$N^+ = NP_e.$$ 

Since $P_f = 1 - P_e$, then

$$N^+/N_o = P_e/(1 - P_e).$$

Williams assumes that the electrons in the sputtering region are at thermal equilibrium (an assumption which he admits "cannot be explicitly defended" but which he contends is reasonable since electron-electron interactions are much faster than atom-atom collisions (Wi79a, p. 620)) so that using Fermi-Dirac statistics:

$$P_e = 1/(1 + \exp(-\Delta E/kT_e)).$$

This implies that:

$$N^+/N_o = \exp(-\Delta E/kT_e)$$

(1.7)
where $T_e$ represents the equilibrium temperature of the electrons and $\Delta E$ is the energy difference between the level in the sputtered atom at energy $I$ and the highest occupied state of the quiescent surface at energy $E_t$. Williams states that the energy $E_t$ is to be thought of as a photoelectron threshold. Therefore, the difference $\Delta E$ for a metal corresponds to the difference between the ionization energy of the sputtered atom and the work function of the surface.

### 1.4.2 Chemical Models

Several models have been proposed to explain all or part of the secondary ion emission features presented in observation #2 above. Included among these are the bond-breaking model of Slodzian (SI75), the molecular model of Thomas (Th77), and the surface polarization model of Williams and Evans (Wi78).

In the bond-breaking model, the observations that the presence of oxygen and cesium at the surface of a metal increases the yield of positive and negative secondary ions, respectively, and that alkali halides emit secondary ions abundantly have been described in terms of the breaking of ionic bonds at the target surface during ion bombardment (SI75). The emission of secondary ions from alkali halides, such as NaCl, under projectile bombardment is qualitatively described as follows. The Na and Cl atoms exist as ions in the lattice of the solid. During ion bombardment, the bonds are destroyed and the Na and Cl atoms are ejected directly as Na$^+$ and Cl$, respectively. For a metallic oxide (MO), a similar process is postulated to occur. Since the electronegativity of oxygen is higher than that of most metals, the breaking of bonds during sputtering yields a positively-charged metal ion and a negatively-charged oxygen ion, $\text{MO} \rightarrow \text{M}^+ + \text{O}^-$. A complementary argument is proposed for ionization in the presence of cesium or other electropositive elements.

The ionization process is, of course, much more complex than suggested by these simplified arguments and may account, in part, for the fact that the bond-breaking model has not been
developed quantitatively. Even qualitatively, however, the model has difficulties in describing the emission of secondary ions from covalent materials and oxides which are only partially ionic in character. In addition, the enhancement in the emission of negative ions during oxygen exposure (Mo73, Wi78) is not predicted by the model.

A similar model of ion formation from metal oxides or from cesiated metallic surfaces has been proposed by Thomas (Th77). In this model, molecules are considered to be emitted intact during ion bombardment. Since the electronic transition rates (<10^{-14} s) are much faster than the emission time of an atom or molecule (>10^{-13} s), Thomas suggested that no excited or ionized species formed at the surface can escape without de-excitation or re-neutralization. As a result, only excited or ionized atoms formed beyond the range of electronic interactions of the surface may be observed. The proposed mechanism of ion formation is as follows. When the sputtered molecule leaves the target surface, it has generally received sufficient energy to dissociate. During the time necessary for dissociation (~10^{-13} s), the system is first compressed, driving the system up the repulsive part of the potential energy interaction curve. Upon relaxation, the potential energy of compression is converted into kinetic energy of the components and they will dissociate. The ionization and excitation of the fragments result from level crossings during the compression of the molecule (Fa65). Although this model also has not been quantified, it does account for the observations of increased yields of positive and negative metallic secondary ions from surfaces exposed to oxygen or cesium, respectively. The enhancement of the yield of negative ions under oxygen exposure (Mo73, Wi78) is more difficult to reconcile with the model because the process MO → M^- + O^+ is not favored energetically.

This problem of both the bond-breaking and molecular models was corrected by Williams and Evans in the surface polarization model (Wi78). For a metallic oxide, this model considers a microscopically heterogeneous surface with the oxygen located either above the surface or below the surface. (Williams and Evans termed these locations as electron-retentive and
electron-emissive sites, respectively.) Since most metals have a lower electronegativity than oxygen, electron transfer results in a surface dipole which increases the potential barrier for electron emission when the oxygen is adsorbed above the surface and lowers the barrier when oxygen is incorporated below the surface. Thus, the yield of positively-charged metal ions will be enhanced with the oxygen situated above the surface and will be reduced with oxygen below the surface. The model does not predict the magnitude of the yield or the charge of the sputtered oxygen, but, based on the above description, it is expected that $O^-$ will be dominant.

1.4.3 Quantum Mechanical Models

A number of quantum mechanical models have been proposed to describe secondary ion emission (Sc73, Sr74, Bi76, Na79, Sr80, Go84). In this section, we will concentrate only on two models: one to describe the emission of multicharged metallic secondary ions (Jo69, Jo73) and the second to explain the enhanced emission of positive secondary ions of electronegative target constituents during keV ion bombardment (Wi81).

Studies of clean Al (He68b) and Si (Ma75) targets under Ar$^+$ ion bombardment have shown that the emission of multiply-charged positive secondary ions increased dramatically as the primary ion energy increased from 1 keV to 15 keV. The yield of singly-charged Si ions was also observed to increase rapidly for Ar energies above ~7 keV. The results of Maul and Wittmaack for Si are shown in Figure 1.3 (Ma75). These results were interpreted by Joyes in terms of a kinetic mechanism of secondary ion formation (Jo69, Jo73).

In this model, some of the collisions that occur during the collision cascade are violent enough to dislodge one of the bound electrons of the atoms. The mechanism for this inner-shell vacancy formation is described by the molecular orbital promotion model of Fano and Lichten (Fa65, Li67). During a collision, the atomic levels of the colliding atoms become molecular levels of the
combined system. The energies of the molecular levels depend upon the distance of approach of the two atoms. For Al and Si at keV bombarding energies, the 2p atomic levels are of interest. As shown schematically in Figure 1.4 (from Wi77b), the 2p levels of the two Al atoms produce four molecular levels in the combined system. The 4fσ level is promoted rapidly as the internuclear separation decreases and its energy crosses into the conduction band. As a result, the 4fσ level becomes a virtual bound state which is no longer well defined but is broadened by its interaction with the continuum. Electrons from this broadened state can escape when the upper energy levels interact with free states above the Fermi energy. Since the interaction time is short, a 2p hole may exist in one of the Al atoms upon separation of the collision partners. (The situation is analogous for Si.) If the lifetime of the vacancy is sufficiently long, the atom may be sputtered in an excited neutral state and, subsequently, Auger decay \textit{in vacuo}. Generally, Auger decay of an excited neutral atom will produce a singly-charged ion and an electron. However, with sufficient electronic excitation energy, a doubly-charged or even a triply-charged ion may be produced (Jo69).

In order to test the kinetic mechanism, studies of secondary electron emission during Ar ion bombardment were performed (He68a, Wi79b). For both Al and Si, the trend of Auger electron emission paralleled that of the low-energy multiply-charged secondary ions. As a result of these observations, multiply-charged secondary ions of Al, Si, and Mg are generally believed to be produced by the kinetic mechanism of Joyes (Wi77b). (We note that Van de Weg and Bierman observed fast multiply-charged Cu secondary ions (>200 eV) which were produced in direct collisions between the projectiles (30 to 90 keV Ar+) and the target atoms (Va69a, b, c)).

Prior to discussing the model proposed by Williams to explain the observations of enhanced emission of low-energy positive secondary ions of fluorine and chlorine from fluorinated Si and chlorinated Al, respectively, under 2-10 keV Ar+ and O2+ bombardment (Wi81), it is necessary to consider the mechanism proposed by Knotek and Feibelman to explain electron-stimulated
desorption (ESD) from maximal-valency ionic solids (Kn78). A maximal-valency solid, such as TiO₂, is one in which the cation is ionized to its noble gas configuration, e.g. Ti⁴⁺, and in which the highest occupied level of the cation is its highest core level with binding energy >20 eV. The anions are negatively ionized to their noble gas configurations, e.g. O²⁻.

In their measurements, Knotek and Feibelman observed that ESD thresholds for O⁺ emission as a function of incident electron energy coincided with the excitation energies of core hole electrons and that the electronegative species was more often desorbed from the surface. To explain these observations, they postulated that an interatomic Auger decay of the core hole was responsible for the desorption of the O⁺ ions. The principles of the mechanism are shown schematically in Figure 1.5. An incident electron knocks an electron out of a core level in the cation of the material. Since the cation is ionized to its noble gas configuration, there are no high-lying electrons available to fill the vacancy. As a result, a valence electron from a neighboring O²⁻ ion falls into the core hole. Subsequently, one or more Auger electrons are emitted from the oxygen ion to release the energy of the decay. If two Auger electrons are emitted, an event which occurs about 10% of the time for TiO₂ (Kn78), the O²⁻ is transformed into an O⁺. The positive oxygen ion is now repelled by the positive cation cores (e.g. Ti⁴⁺) and, if the oxygen is on the surface, it will desorb as an O⁺ ion.

The Knotek-Feibelman mechanism works equally well when core holes of the anion of a maximal-valency solid are produced. In this case, an intraatomic Auger decay produces the O⁺ ion which is subsequently repelled by the positive cation cores. In contrast, the model predicts that non-maximal valency ionic solids, such as Ti₂O₃, should not desorb O⁺. In a discussion of this prediction, two possible desorption mechanisms must be considered. First, if a core hole is produced on the cation, there exist valence electrons on the cation to fill the vacancy. Thus, the cation will become more positively-charged but this does not necessarily represent a repulsive environment for the oxygen ion. Second, if the core vacancy is formed on the anion, a multiple
valence-hole final state will result from the intraatomic Auger decay. This should lead to desorption as in the maximal valency case. However, no desorption was observed (Kn78, Kn84a) and it was postulated that the free electrons on the surrounding cations enhanced the re-neutralization and re-capture of the positive anion (Ku84).

We conclude this discussion of electron-stimulated desorption by noting that enhanced emission of low-energy positive secondary ions of electronegative target constituents has also been observed during electron bombardment of covalent materials. The desorption is known to proceed by essentially the same mechanism as that for maximal valency ionic solids (Fr79). For a more complete discussion of this process, the reader is referred to a recent review article of Knotek (Kn84a).

We now discuss the model proposed by Williams to explain his observations of enhanced emission of F⁺ and Cl⁺ secondary ions during 2-10 keV Ar⁺ and O₂⁺ bombardment of fluorinated Si and chlorinated Al, respectively. For the fluorinated Si target, it was determined that the F⁺ ionization probability exceeded that of Si⁺ by more than a factor of thirty even though the ionization potential of F was more than twice that of Si. This was in direct contradiction to the general observation that secondary ion yields of elements sputtered from a common matrix exhibited an inverse exponential dependence on the ionization potential of the sputtered atom. Also, the energy distribution of the F⁺ ions showed that essentially all the fluorine ions had energies below 20 eV (Figure 1.6a) while the Si⁺, Si⁻, and F⁻ ion energy distributions were typical of keV ion bombarded solids. Williams noted the similarity of the F⁺ energy distribution to that generated by 14.5 keV electron bombardment of the sample (Figure 1.6b). This similarity to ESD results and the observation that, for ion bombardment, the F⁺ secondary ion yield scaled with the yield of Si²⁺ and with the Si (LVV) Auger electron yield (Wi79b, Wi81) prompted Williams to propose the following model for the emission of positive ions from the electronegative species. The F⁺ secondary ions were postulated to be produced as a result of true ESD events of the Knotek-Feibelman type (Kn78) triggered by a collisionally-produced silicon LVV Auger electron from a silicon atom which
was not a nearest neighbor of the emitted fluorine atom. Williams justified this geometric conclusion by reasoning that the low energies of the F+ ions implied that the core hole necessary for the Knotek-Feibleman mechanism could not have been produced directly in the fluorine atom through an atomic collision. The Si LVV Auger electron could not have come from a nearest neighbor Si atom for the same reason.

This model of secondary ion formation, which Williams termed ion-stimulated desorption (Wi81), provides a good description of his observations of enhanced emission of positive secondary ions of electronegative target constituents during keV ion irradiations. However, he notes that such observations are rare during keV ion bombardment. Our measurements have tested the applicability of this model, as well as each of the models discussed in this section, to secondary ion emission during MeV projectile irradiations where significant electronic excitation of the sputtering region occurs.
Figure 1.1 Schematic representation of the three qualitatively different regimes of collisional sputtering: (a) the single knock-on regime, (b) the linear collision cascade regime, and (c) the spike regime. (From (Si81)).
Figure 1.2 Schematic representation of the surface electronic excitation model.

The probability that a sputtered atom has an electron in the energy level, $I$, is assumed to be equal to $P_I$, the probability that the corresponding level in the surface is occupied. Similarly, $P_e$ is the probability that the level in the surface is empty. $E_t$ is a photoelectron threshold which corresponds to the work function in a metallic target. (From (Wi79a)).
Electron Energy Distribution

Surface Potential Energy Diagram

Pe - Pf

$E_T$

I
Figure 1.3 The projectile energy dependence of secondary ion intensity obtained from a clean Si surface (doped with 600 ppm B) during Ar$^+$ ion bombardment (From (Ma75)).
Secondary Ion Intensity (counts/s)

![Graph showing secondary ion intensity vs. energy](image)

- SiO⁺
- B⁺×10²
- Ar⁺-Si (600 ppm B)
- j=84Å/cm²
- p(O₂)=2×10⁻¹⁰ Torr

Energy (keV)
Figure 1.4 Schematic representation of electron promotion in Al-Al collisions (From (Wi77b)). (The curves are interpolated from diagrams for Ne-Ne and Ar-Ar collisions (Li67)).
**Figure 1.5** Schematic representation of the interatomic Auger decay process in a maximal-valency ionic solid. Core holes created on either ion decay to the Fermi level by hole multiplication to selectively remove electrons from the anion. (From (Kn84b)).
Figure 1.6 (a) Energy distributions of F\(^+\) and \(^{30}\text{Si}^+\) secondary ions emitted from a fluorinated amorphous silicon sample during 8 keV Ar\(^+\) bombardment. (b) Energy distribution of F\(^+\) secondary ions ejected from the same sample during 14.5 keV electron bombardment (As a result of the experimental technique used to measure the energy distributions, secondary ions formed in the gas phase appear in the spectra with negative kinetic energies.) (From (Wi81)).
ION SIGNAL (counts/sec) vs. KINETIC ENERGY (eV)

- 30Si⁺
- F⁺

(a) and (b) panels show different energy distributions.
CHAPTER 2
SECONDARY ION MASS SPECTROMETRY

2.1 General Description of Measurements

Positive secondary ion mass spectra were measured using a quadrupole mass spectrometer both with an energy pre-filter of novel design (Oc83, Oc85a, Bl85a) and a commercial electrostatic energy analyzer (Kratos Analytical, Inc.). Preliminary measurements, using an initial version of the energy pre-filter, were performed using Cu, Nb, and Ta targets bombarded by 75 MeV $^{79}\text{Br}^{8+}$ projectiles (Oc83). The purpose of these measurements was to determine if ions of the metal were being sputtered in detectable quantities and to measure the amount of surface contaminants relative to the metal ions from the substrate. A 75 MeV Br beam was chosen for two reasons. First, for many targets, the electronic stopping power was near maximum (No70, Zi80) while the nuclear stopping power was large enough to produce collisional sputtering yields between 0.1 and 1.0 (estimated using eq. (1.1)). Second, relatively intense beams of these ions may be conveniently produced in a tandem Van de Graaff accelerator.

Using an improved version of the energy pre-filter, mass spectra were obtained from Al, Ti, V, and Ni foils during 70 MeV $^{79}\text{Br}^{7+}$ and 100 keV $^{40}\text{Ar}^+$ ion bombardment (Oc85a). The specific goal of these measurements was to identify those spectral features that were most affected by the change in projectile energy. Subsequently, the variation of the yields of $\text{O}^+$, $\text{F}^+$, $\text{V}^+$, and $\text{VO}^+$ secondary ions sputtered from a V target by 10-90 MeV $^{79}\text{Br}$ projectiles was measured in order to determine the systematics of the ionization process (Oc85b).

Measurements of the variation of secondary ion yields were continued using the commercial electrostatic analyzer. In these experiments, Al, V, and Y surfaces were bombarded by 2.8-40 MeV $^{79}\text{Br}$ projectiles. Positive secondary ion emission was studied both as a function of beam energy and as a function of deposited charge. The final measurements were performed using Al and V
targets bombarded by 50, 100, and 250 (V only) keV $^{79}$Br projectiles. These measurements were
designed to obtain a quantitative comparison of secondary ion intensities measured using keV and
MeV projectiles.

In this chapter, the instruments and procedures used during these measurements are
discussed. This is followed by a presentation of the results and an evaluation of quantifiable
uncertainties. We begin by describing the accelerators, vacuum chambers, and targets used during
the experiments.

2.2 Accelerators, Vacuum Hardware, and Targets

Two sources of primary ions were used during these experiments. For the high energy
measurements, $^{79}$Br beams were generated by a Middleton-type Cs ion source (Mi74) and injected
into the Yale MP-1 tandem Van de Graaff accelerator (housed at the Wright Nuclear Structure
Laboratory (WNSL).) After acceleration, the ion beam was momentum analyzed by a 90° bending
magnet and directed by a switching magnet into the R30 beam line. Br energies ranged from 2.8 to
90 MeV. The beams were focused to a spot of approximately 3 mm$^2$ in area and ranged in charge
states from 2$^+$ for 2.8 MeV to 8$^+$ for the 90 MeV projectiles. Beam currents were typically in the
range of 4-60 nA. The pressure downstream of the switching magnet was between 10$^{-6}$ and 10$^{-7}$
Torr. A differentially-pumped beam line (Figure 2.1) was assembled to lower this pressure to
conditions in the scattering chamber which were suitable for surface analysis. The pumping
elements were two Ultek 150 l/s ion pumps, a liquid nitrogen cooled in-line cold trap (40 cm long
with a 1 cm inner diameter), a 220 l/s ion pump and titanium sublimation pump. The latter two
elements were mounted below a custom 12" diameter bell jar manufactured by the Vacuum
Products Division of Perkin-Elmer. The ion pump downstream of the cold trap was used in a novel
manner following the work of Griffith (Gr79). The pump was mounted on the beam line so that the
beam would pass through its central section. The magnetic field in the interior of the pump was
estimated to be less than 30 Gauss in the central region (Perkin-Elmer, Ultek Inc., Ion Pump Manual, C-1542). A field of this size would deflect the beam at most 0.25 mm at the target. No problems were encountered in steering the beam through the pump. The bell jar was used to house the targets and the detectors. In addition, a 3 keV Ar ion gun (Varian Industrial Products, Model 981-2043) and a leak-valve controlled source of research grade Ar (<5 ppm impurities) (Cryc-Dyne Corp., Classification No. UN1006) were mounted on the vacuum chamber. The system was isolated from the rest of the beam line by a copper-sealed straight-through valve. With the valve closed and following a bakeout at 150 °C for about a week, a base pressure of \(\sim 7 \times 10^{-11}\) Torr was obtained. During measurements, typical pressures ranged from \(3 \times 10^{-10}\) to \(1 \times 10^{-9}\) Torr.

For the low energy measurements, 50-250 keV \(^{79}\)Br\(^+\) and 100 keV \(^{40}\)Ar\(^+\) projectiles were produced by a 300 kV Cockcroft-Walton accelerator at WNSL. These beams were momentum analyzed and directed into the differentially-pumped beam line shown in Figure 2.2. The pressure at the analyzing magnet was typically 1 to \(5 \times 10^{-6}\) Torr. This high pressure was principally a result of Ar gas from the ion source which was situated only about 2 meters upstream of the magnet. The pressure was lowered to ultra-high vacuum (UHV) conditions by a liquid nitrogen cold trap similar to that on the tandem accelerator's beam line, a Varian 220 l/s ion pump, and an Ultek 220 l/s ion pump mounted beneath a 12° scattering chamber. This system also had a base pressure of \(\sim 7 \times 10^{-11}\) Torr. Typical pressure during experiments was \(5 \times 10^{-9}\) Torr.

The targets used in these measurements were cold-rolled polycrystalline foils of Al, Ti, V, Ni, Cu, Y, Nb, and Ta with purities ranging from 99.9% for Y to 99.999% for Al (Alfa Products, Thiokol-Ventron Division). Prior to introduction into vacuum, they were degreased in trichlorotrifluoroethane (freon TF), rinsed in warm distilled water, rinsed in reagent-grade isopropyl alcohol, and hot-air dried. As noted, the UHV systems including the targets were baked at 150 °C for several days prior to data collection.
2.3 Quadrupole Mass Spectrometry

The quadrupole mass filter, which was introduced by Paul and co-workers (Pa53), was the first of the path-stability mass spectrometers. The basic principles of the analyzer are shown schematically in Figure 2.3a. An alternating potential, $V \cos \omega t$, is superimposed on a direct voltage, $U$, and the resulting potential, $\Phi$, is applied to the quadrupole rods as illustrated. An ion entering the region between the rods in the $z$-direction will be alternatively focused and de-focused in both the $xz$ and $yz$ planes. For a given value of the period of the sinusoidal voltage, only ions with a mass-to-charge ratio within a well-defined range will follow stable trajectories and be transmitted to the detector (three examples are shown in Figure 2.3b). All other ions will follow unstable paths with oscillations of increasing amplitude until they strike the rods or the housing. A measurement of a mass spectrum consists of counting the number of particles that pass through the quadrupole region as the applied voltages ($V$ and $U$) are swept through a preset range with the ratio of these voltages held constant. The width of the mass range of stable trajectories is determined by the ratio of the direct component of $\Phi$ to the alternating component. Since the sensitivity (resolution) of the mass filter is directly (inversely) proportional to this width, tradeoffs between sensitivity and resolution are obtained by simple adjustments to the RF/DC voltage ratio. Also, it is noted that the filtering action of the quadrupole is relatively insensitive to the energy of the analyzed particle, provided that the length of the quadrupole field is long enough. Mathematically, the motion of the ions is described by the Mathieu equation. For a detailed discussion of this equation and its solutions, the reader is referred to the work of Dawson (Da74, Da75, Da76a).

Quadrupole mass analyzers have several advantages over magnetic sector spectrometers. They are relatively inexpensive, compact, lightweight, and mechanically simple. In addition, they are capable of high-speed electronic switching with a linear mass scale. However, a compact
quadrupole mass filter is limited in its application to the study of secondary ions. Measurements of sensitivity versus mass resolution (Ho72) indicate that only low energy (about 4-10 eV) ions may be analyzed with both high resolution and high sensitivity. Although typical secondary ion energy distributions obtained with keV projectiles peak in this energy range, they exhibit slowly decreasing high energy tails (Bl79). These fast ions cannot be fully analyzed but may still reach the detector. In addition, sputtered neutral particles and high-energy backscattered primary ions will enter the mass filter and create ions in collisions with either the quadrupole rods or the housing. A fraction of these ions may also reach the detector. This results in a substantial background signal and a tailing on the low-mass side of the mass peaks (Da74, Wi73). Therefore, it is necessary to enforce limits on the energy of ions entering the quadrupole field in order to maintain satisfactory resolution. This is most commonly accomplished by requiring that the ions pass through an electrostatic energy analyzer before entering the quadrupole fields (See Wi82b for a detailed review of these techniques). In our measurements, we have used a quadrupole residual gas analyzer with both an unconventional approach to energy selection and with a standard commercial electrostatic energy pre-filter. These instruments and procedures are described below.

2.4 Quadrupole Mass Filter

The quadrupole mass filter used in these experiments was part of a commercial residual gas analyzer (Utthe Technology Inc., Model 100C). Operating at a frequency of 2 MHz, it had a mass-to-charge (M/q) range of 1-300 u/e. The control unit of the analyzer was designed to accept a 0-10 V signal from an external source which would sweep the quadrupole through the 1-300 u/e mass range. All the measurements described below used this input to permit computer control of the experiments. Nominal mass resolution of the analyzer was 1/2 u/e FWHM. However, by adjusting the RF/DC ratio applied to the rods, either high resolution (up to 1/10 u/e FWHM) or high sensitivity was obtainable. Transmission through the quadrupole was quoted by the manufacturer
to be 100% for ions with $M/q \leq 40 \text{ u/e}$ but to decrease at a rate of approximately one decade per 150 u/e (Figure 2.4). The drop in transmission is a result of the fact that heavier ions at a given energy spend a greater number of RF cycles in the quadrupole field than light ions and, as a result, are more likely to be discriminated against. Ions that were transmitted through the quadrupole field were detected by an off-axis channel electron multiplier (CEM) (Galileo Electro-Optics Corp., Model 4717). The efficiency of the channeltron varied approximately as the inverse square root of the mass of the detected ion (Ku79).

2.5 Ion Energy Selection by Voltage Modulation

2.5.1 General Technique

As noted in Section 2.1, an unconventional method of energy selection of the secondary ions was used during several of the measurements of secondary ion mass spectra. This technique, developed by P. Blauner (Oc83, Oc85a, Bl85a), was an adaptation of the analog modulation technique employed by Thomas and de Kluizenaar (Th74) and by Lundquist (Lu78). These authors applied a sinusoidal voltage to an electrode in front of the mass filter entrance to modulate the intensity of the low energy ions which entered. Using a lock-in amplifier, they were able to differentiate the low-energy ion contribution to the detector output. The resulting mass spectra were improved significantly over those obtained with a bare mass filter both with respect to the background level and the peak shape. A disadvantage of this procedure is that it cannot be used for single-particle counting which is necessary to achieve high sensitivity (Wi82b). To permit single-particle counting, we have extended this analog technique to a digital one (To82).

The experimental geometry used during the preliminary measurements of mass spectra from Cu, Nb, and Ta targets bombarded by 75 MeV $^{79}\text{Br}^{8+}$ ions is shown schematically in Figure 2.5. Secondary ions emitted from the target passed through the reflector and the grid of the ionizer that was originally mounted on the residual gas analyzer and an aperture in the quadrupole's focus plate.
(not shown) prior to entering the quadrupole field. The target, reflector, and focus plate were maintained at ground potential and a square wave potential was applied to the grid. This produced a time-varying potential barrier that selectively rejected ions within an energy range defined by the high, \( V_{\text{high}} \), and low, \( V_{\text{low}} \), voltage values applied to the grid. At each mass, ions that passed through the energy pre-filter and the quadrupole were detected by the channeltron operating in pulse counting mode. By subtracting those counts obtained when the voltage was high from those obtained when it was low, a mass spectrum of the secondary ions with energies \( E \) such that \( qV_{\text{high}} \leq qV_{\text{low}} \) (where \( q \) was the ion charge) was acquired.

Figure 2.6 shows a schematic diagram of the improved version of the pre-filter used during the survey of targets under 70 MeV \(^{79}\text{Br}^+\) and 100 keV \(^{40}\text{Ar}^+\) bombardment and for the measurement of the variation of secondary ion yields from V bombarded by 10-90 MeV \(^{79}\text{Br}\) projectiles. The ionizer at the entrance to the mass filter was replaced by the structure shown. Secondary ions emitted in a small cone (<4 msr) normal to the target surface passed through a set of collimators, a planar grid, and the focus plate aperture before entering the quadrupole field. The target, collimator, and focus plate were kept at ground potential and the square wave potential was applied to the grid. Mass spectra were obtained in the same manner as discussed above.

### 2.5.2 Data Acquisition

The data acquisition during MeV ion bombardment was a two-step process. The first step was to process the signals from the channeltron. The second was to control the square wave potential applied to the grid and the rate of stepping through a pre-selected mass range of the spectrometer.

As shown in Figure 2.7, the signals from the channeltron were pre-amplified, amplified, converted into a logic pulse, and counted in a scaler. Beam current was digitized by a Brookhaven
Instruments Corp. Model 1000 integrator and similarly counted. (No secondary electron suppression was applied to the target in order to avoid perturbing secondary ion trajectories.) The scaler outputs were sent to the laboratory's IBM 4341 computer by the Front End (Nu67), an interfacing device. Using the Data Acquisition Language (DAL), three multichannel scalers were created in software for storage of the mass spectra obtained with grid voltage low and high and for the difference.

During a measurement, the modulation grid voltage began at its low value. After a fixed amount of collected charge, a logic pulse from the beam current scaler would be generated. This signal had two purposes. First, it would trigger the differential pulse generator to switch the grid voltage from its low to high value. In addition, this pulse would serve as an event trigger and would be sent to a special input of the Front End where it would send an instruction to the computer to read the two scalers and store the data in the "low" multichannel scaler. Counts would then be collected for the same amount of charge with the grid voltage at its high value and the data stored in the "high" multichannel scaler. When this was completed, the channel was advanced, the grid voltage was switched back to the low value, and the ramp voltage (applied to the external input of the spectrometer's control unit) was stepped to its new value. (For these measurements, the ramp voltage was generated by an Ortec 487 Spectrum Scanner.) Typical dwell times per channel were 30 to 300 ms. At the end of a measurement, two mass spectra corresponding to the grid voltage high and low had been obtained.

For keV ion bombardment, the procedure was similar (Figure 2.8). The data acquisition and storage were controlled by a PDP 11/23 computer. The signals from the channeltron were pre-amplified and counted in a multichannel analyzer (Canberra Series 40) operating in multichannel scaler mode. The counts obtained with the grid voltage low and high were stored in different memory areas of the analyzer. A digital-to-analog converter (DAC) was used to generate the control voltage for the mass spectrometer. Beam current was digitized using the Brookhaven integrator. The logic signals from the integrator were used to generate interrupts for the PDP 11/23 computer.
A programmed number of interrupts, i.e. a set amount of collected charge, determined when the grid voltage would change and the DAC would advance to a new value. Mass spectra were obtained by stepping the DAC voltages through a preset range.

2.5.3 Measurements and Results

2.5.3.1 Preliminary Measurements

Positive secondary ion mass spectra were measured using a 0-10 V modulation voltage for Cu, Nb, and Ta targets bombarded by 75 MeV $^{79}$Br$^{8+}$ projectiles. Mass spectra were obtained both before and after 1/2 hour of sputter cleaning in situ with 3 keV Ar with a current density of $\sim$3μA/cm$^2$. This cleaning procedure was estimated to remove about 50 monolayers of material from the surfaces (An81). In addition, the Nb and Ta targets had been sputter etched for two hours using 3 keV Ar and exposed to approximately 500 L of residual gas prior to the measurements (1 Langmuir=1L=10$^{-6}$ Torr-sec). During the measurements, the Br beam was incident at an angle of 45° with respect to the surface normal and secondary ions were detected at an angle of 30°.

The results are shown in Figures 2.9-2.11. The spectra that are presented have not been corrected for quadrupole transmission and channeltron efficiency since these quantities are only approximately known. Also, ion optical effects resulting from the voltage modulation have not been included. (These effects are discussed in the Section 2.5.3.3.) In addition, in comparing these spectra with other published spectra, it must be remembered that only ions in the energy range 0-10q eV (where q was the ion charge) were collected.

In these figures, we clearly see evidence of sputtering of the metals by the high energy projectiles. (The small intensity of the Ta$^+$ signal is deceptive because of the lowered transmission of the quadrupole and lower efficiency of the channeltron. If these effects are included, I(Ta$^+$) is estimated to be approximately equal to I(O$^+$).) In addition, a significant number of low-mass peaks are present on all mass spectra obtained before sputter cleaning. The most prominent of these on
each spectrum are $^1\text{H}^+$ and $^{16}\text{O}^+$. By comparing the spectra obtained from the Cu foil before and after sputter cleaning, it is evident that most of these spectral features may be attributed to sputtered or desorbed surface contaminants. The absence of all features except $\text{H}^+$ and the Cu isotopes on the spectrum obtained from the cleaned Cu target demonstrates that the observed secondary ions are correlated with the surface of the target and are not instrumental artifacts. With the exception of a trace amount of NbO$^+$ observed in the spectrum of Figure 2.10a, evidence of sputtered metallic oxides was surprisingly absent from the spectra.

This absence and the large abundances of $^{12}\text{C}^+$ and $^{16}\text{O}^+$ ions are the most striking differences between these spectra and those obtained with keV projectiles. In particular, the presence of substantial numbers of positive secondary ions from electronegative surface constituents is in direct contrast to the observation that, for keV projectiles, the yield of ions sputtered from a common matrix exhibits an inverse exponential dependence on the ionization potential of the ejected atom. Müller and Benninghoven have studied the emission of secondary ions from clean and oxidized Cu ($\text{Mü74}$), Nb, and Ta surfaces ($\text{Mü73}$) during 3 keV Ar ion bombardment. For the Cu target, no $^{16}\text{O}^+$ ions were observed from either the clean or oxidized surfaces. This is to be contrasted with the large O$^+$ signal seen in Figure 2.9a. For oxidized Nb and Ta targets, an O$^+$ signal comparable to that of Nb$^+$ and Ta$^+$ was observed. However, this was accompanied by a large increase in the emission of metal oxide ions. The intensities of NbO$^+$ and TaO$^+$ ions were about a factor of six larger than that of O$^+$. In addition, $I(\text{NbO}_2^+)$ and $I(\text{TaO}_2^+)$ were about a factor of two larger than $I(\text{O}^+)$. 

The results shown in Figures 2.9-2.11 may also be compared to results obtained by Wien and collaborators who have also studied secondary ion emission from metallic surfaces during MeV ion bombardment by time-of-flight mass spectrometry ($\text{Kr78, Kn82, Be83a}$). In the comparisons made with their data, however, it is important to note that their apparatus collected all secondary ions with energies below 300 eV/q. The data presented here contain only ions emitted in a small solid angle with energies determined by the low and high modulation voltage values. Differences in the
secondary ion energy distributions of the emitted species will result in quite different values of such ratios as \( I(O^+)/I(M^+) \) in the two sets of measurements. Krueger and Wien have studied ion emission from sputter-cleaned Al, Ni, and Cu foils bombarded by \(^{252}\text{Cf}\) fission fragments (Kr78). In the positive ion mass spectrum obtained from the Cu target, they observed the Cu isotopes as well as significant amounts of \( \text{H}^+, \text{H}_2^+, \text{Na}^+, \text{K}^+ \), and a peak at 51 u/e. In comparison, only peaks corresponding to hydrogen and the Cu isotopes are observed in the spectrum presented in Figure 2.9b.

Becker, Knippelberg and Wien (Be83a) have also recently studied ion emission from sputter-etched Al, Sc, Y, and Ta surfaces using \(^{58}\text{Ni}\), \(^{132}\text{Xe}\), and \(^{238}\text{U}\) projectiles in the velocity range 0.2-1.4 cm/ns. (The velocity of a 75 MeV Br ion is 1.35 cm/ns.) In the spectrum obtained from Ta bombarded by Xe at a velocity of 1.25 cm/ns, substantial numbers of \( \text{H}_2^+, \text{H}_3^+, \text{C}^+, \text{O}^+ \) secondary ions were observed. Significant quantities of Ta\(^+\) and TaO\(^+\) ions were also observed with \( I(\text{Ta}^+) \) exceeding \( I(\text{TaO}^+) \) by approximately a factor of six. In addition, a very large number of \( \text{H}_1^+ \) ions were observed (\( I(\text{H}_1^+) \approx 50 I(\text{Ta}^+) \)). The large abundances of \( \text{H}^+, \text{C}^+, \text{O}^+ \) are in qualitative agreement with the results presented in Figure 2.11b. Also, the small \( I(\text{TaO}^+)/I(\text{Ta}^+) \) ratio observed by Becker et al. is consistent with the absence of TaO\(^+\) ions in our measured spectrum since the intensity of Ta\(^+\) ions was also quite small.

2.5.3.2 Comparison of Secondary Ion Emission During 70 MeV \(^{79}\text{Br}^7+\) and 100 keV \(^{40}\text{Ar}^+\) Bombardment

Since the initial measurements showed that mass spectra obtained during MeV ion bombardment had several interesting features including large yields of positive secondary ions of electronegative target constituents, especially \( \text{O}^+ \), mass spectra were measured using the improved energy pre-filter from similarly-prepared Al, Ti, V, and Ni targets during 70 MeV \(^{79}\text{Br}^7+\) and
100 keV 40Ar\(^+\) projectile bombardment. These experiments were designed to identify those spectral features that were most affected by increasing the projectile energy.

Prior to the measurements, the system was tested using an indirectly-heated Na ion source (Spectra-Mat, Inc., Model 600) to obtain mass spectra of ions of known initial energy and mass. With the modulation grid maintained at ground potential, the FWHM of the Na\(^+\) peak was observed to increase linearly with ion energy in the range 5-100 eV (Bl86). Since the mass resolution of the system became unacceptable for ions above 40 eV (3/4 u/e FWHM for 40 eV Na\(^+\) ions), the grid was set to switch between voltages \(V_{\text{low}}=0.1\) V and \(V_{\text{high}}=40.0\) V.

Samples receiving MeV ion irradiation were first sputter etched with 3 keV Ar to remove about 50 monolayers of material from the surfaces. This was not adequate, nor intended, to produce atomically-clean surfaces (Mu82). Rather, it was intended to compensate for the larger sputtering yield of 100 keV Ar during the low energy measurements. Since the Br beam spot was \(~0.2\) cm in diameter, and since (for keV projectiles) the presence of unsputtered oxide layers at the periphery of the primary ion beam may produce anomalously high yields of atomic metallic secondary ions (Be72, Wi79a), an area of 1 cm\(^2\) was pre-sputtered in order to minimize these edge effects. During the measurements with 70 MeV Br projectiles, the total amount of material removed was estimated using eq.(1.1) to be less than one monolayer. The 100 keV Ar beam was used to briefly sputter the targets prior to the low energy measurements. The amount of material removed during this procedure was 2-3 monolayers for Al and Ni, and 25 monolayers for Ti and V. Additionally, 3-6 monolayers were removed during the measurements. The Br and Ar beams were incident at angles of 30\(^\circ\) and 45\(^\circ\), respectively, with respect to the surface normal during the measurements.

The positive secondary ion mass spectra obtained during the experiment are shown in Figures 2.12-2.15. Table 2.1 presents the relative intensities of metal, oxygen, and metal oxide ions with the data for each target normalized to \(M^+=100\) and with the Ar and Br projectile data individually normalized. Prior to discussing the spectral features, we note that only ions within the
energy range (0.1-40)\,\text{eV} were included and that, as previously, no correction for quadrupole transmission was applied. In general, this energy range appears to include \(>90\%\) of all surface contaminant ions, metal oxides, metal complexes, and multiply-charged metal ions, but substantially fewer of the singly-charged metal ions (M\(^+\)). The number of ions with energies exceeding the 40 eV range may be estimated by comparing the number of counts (integrated over all masses) in the (0.1-40)\,\text{eV} energy band with the total. For the Al target, it was determined that 76\% of all ions fell in the 0.1-40 eV band during 70 MeV Br bombardment while this ratio dropped to 31\% during 100 keV Ar bombardment. While some of this difference may be attributed to more backscattered particles during the low energy measurements, a significant portion is the result of an upward shift in the energy distribution of the Al\(^+\) ions. This shift is clearly reflected in the widths of the Al\(^+\) peaks in Figure 2.12. Since the resolution of the mass spectrometer decreased with increasing energy of the analyzed ions, the Al\(^+\) peak in the spectrum obtained during 100 keV Ar irradiation is noticeably wider than the corresponding peak in the spectrum from 70 MeV Br irradiation. A similar, though less pronounced, effect may be seen for the other M\(^+\) ions. In contrast, the Na\(^+\) peaks in spectra obtained from V (Figure 2.14) have widths that are equal within statistical error. This is because in each case the Na\(^+\) ions are relatively low in energy. The observed tendency for higher background in the spectra from the 100 keV Ar irradiations is also attributable to the smaller fraction of ions with analyzable energies.

Several interesting similarities and differences are seen in a comparison of the spectra obtained with the 100 keV Ar and 70 MeV Br projectiles. First, M\(^+\) ions were the dominant species emitted during the 100 keV Ar irradiations. Substantial numbers of M\(^+\) ions were also observed during MeV ion bombardment. The intensity ratios of the metal oxide to metal ions emitted from the Al, Ti, and V targets were also similar during the Ar and Br irradiations. NiO\(^+\) ions were not observed at either beam energy.

Significant differences were observed in the emission of secondary ions from surface contaminants. During MeV ion bombardment, an intense \(^{16}\text{O}^+\) signal was observed from each
target which was comparable to (Al, V, Ni) or substantially greater than (Ti) the intensity of the M+ ions. In contrast, O+ ions were not detected from the Al, Ti, or Ni targets and only a small number of O+ ions were observed from the V target during the 100 keV Ar irradiations (Table 2.1). Also, the O+ ions observed during MeV ion bombardment had very low energies. This is evident from the narrow peaks in the mass spectra. By using a modulation voltage range of 0-20 V, it was further determined that an upper limit on the energy of the O+ ions could be conservatively placed at 20 eV.

Several other surface contaminants observed during MeV ion bombardment were not seen during 100 keV Ar bombardment. These include a significant amount of mass 19 u/e, probably 19F+, a residue of the cleaning process. Also, H+ and H2+ ions are clearly distinguished in all spectra and H3+ ions are statistically significant in the spectra of the Ti and V targets. Note, in addition, the presence of mass 32 u/e, a likely superposition of 32S+ and O2+, in the Ti and V spectra and also 35Cl+ and 37Cl+ in the Ti spectrum. These contaminants (Cl and S), which previously have been reported as common in these metals (Mu82), were absent in the 100 keV Ar data.

The final difference of note was the observation of 27Al2+, 27Al3+, and 16O2+ in the Al spectrum obtained during 70 MeV Br bombardment (Table 2.1). This observation is consistent with the trend in our data toward increased production of singly-charged ions from species with high ionization potentials and with the interpretation that these may result from the Auger decay of inner shell vacancies produced either by the incident projectiles themselves, in a collision cascade, or by energetic secondary electrons.

The large yield of Al2+ secondary ions was particularly interesting since the production of these ions during keV projectile bombardment is believed to be the result of the Auger decay of 2p holes created during the collision cascade (Jo69, Jo73, Section 1.4.3). The intensity ratio I(Al2+)/I(Al+) has been measured by a number of authors (He68b, Ju68, Br71, Ca71, Wi75b, Ba76a,
Da76b, Wi77b, He84) using keV Ar projectiles and has been found to vary from about 0.01% (Ba76a) up to ~10% (He84) depending on surface conditions, the energy of the primary projectiles, and the instrument used for measurement. The larger values in this range are usually associated with surfaces which are free of oxygen. Since we observed an $I(Ai^{2+})/I(Ai^+) \approx 20.5\%$ in conjunction with an intense $^{16}O^+$ signal, the same mechanism which is enhancing $O^+$ emission may be also enhancing $Ai^{2+}$ emission. This is discussed further in Section 2.6.3.

It is interesting to compare the 100 keV Ar data presented in Figures 2.13-2.16 with the results of Müller and Benninghoven who have studied ion emission from clean and oxidized V (Mü73), Ti, and Ni surfaces (Mü74) during 3 keV Ar ion bombardment. For the oxidized Ti and V targets, they measured comparable yields of metal and metal oxide (MO+) secondary ions while no NiO+ ions were observed. In addition, O+ ions were not detected from either the Ti or Ni targets and only a small number were observed from the V target ($I(O^+)/I(V^+) < 0.5\%$). The differences between the $I(MO^+)/I(M^+)$ ratios for Ti and V presented in Table 2.1 and the results of Müller and Benninghoven were probably a result of the use of naturally-occurring oxide surfaces in our measurements. The recent results of Blauner et al. (Bl85b), who measured an intensity ratio $I(VO^+)/I(V^+) = 1$ from a deliberately-oxidized V surface during 100 keV Ar bombardment, lends support to this argument.

It is also instructive to compare our 70 MeV Br data for Al and Ni with the work of Wien and collaborators (Kr78, Kn82, Be83). There is a general consensus on the presence of $H^+$, $H_2^+$, $Na^+$, $K^+$, and $M^+$ ions. Approximately similar ratios of $I(Ai^{2+})/I(Ai^+)$ and $I(Ai^{3+})/I(Ai^+)$ have also been observed. In addition, Krueger and Wien observed a small $^{12}C^+$ signal from the Ni target and a significant signal at 19 u/e from the Al target. However, the oxygen data are less consistent. Knippelberg et al. (Kn82) and Becker et al. (Be83a) have apparently expended substantial effort in preparing clean Al surfaces. The virtual disappearance of $Na^+$ and $K^+$ ions, as well as the elimination of the signal at 19 u/e attest to their success. This would explain the observation of only trace $O^+$
signals in their data. However, while O\(^+\) exceeds Ni\(^+\) in intensity in the data of Krueger and Wien (Kr78), it is absent in the Al spectrum even though substantial Na\(^+\) and K\(^+\) ions are present there. Given the similarities in our data and those of Krueger and Wien, including a similar ratio of \(I(\text{AlO}^+)/I(\text{Al}^+)\), this difference is surprising. Noting that a substantial \(^{12}\text{C}^+\) peak is present in their Al data, it is likely to be attributed to the difference in the level of hydrocarbon contamination on the surfaces.

2.5.3.3 Analysis of Uncertainties

In principle, the background subtraction achieved by the voltage modulation technique statistically eliminated all ions of undesired energies from the mass spectra. However, there are two primary limitations of an energy pre-filter with this design. First, if the spectra being subtracted have a comparable number of counts in a particular region of interest, the large statistical error in the difference will diminish the apparent gain in sensitivity achieved through pulse counting. Second, the rear collimator, the planar grid, and the focus plate of the improved pre-filter form a three element lens whose focusing properties are different when the grid voltage is at its low and high values. (The reflector, grid, and focus plate were the elements of the lens during the preliminary measurements.) When the grid voltage is at its high value, \(V_{\text{high}}\), secondary ions with energies greater than \(V_{\text{high}}\) will be defocused in the retarding field and the acceptance of the lens-quadrupole system will be reduced. Since a comparable reduction will not occur when the grid is low, an undersubtraction of ions with energies \(E > qV_{\text{high}}\) will occur. This effect was investigated using the Na\(^+\) ion source. With a 40 V bias on the grid, Na\(^+\) ions with energies below 40 eV were rejected with approximately 99% efficiency. For ion energies above 40 eV, defocusing by the grid was confirmed to result in an undersubtraction which resulted in an artifact in the difference spectrum. For example, for 45 eV Na\(^+\) ions, the count rate with the grid voltage high was only 18%
of its value when the grid voltage was low. (For a full discussion of the measurement, see (BI86).) Therefore, the utility of the voltage modulation technique for energy selection depends strongly on a favorable energy distribution of the secondary ions. Conversely, as discussed for the 100 keV Ar irradiations, the quality of the background subtraction and the widths of the mass peaks serve as indications of the secondary ion energy distributions.

The lens effect was most significant for low masses because the small quadrupole fields did not fully differentiate with respect to the mass of the secondary ions. For 70 MeV Br bombardment, the error was negligible for all masses except \( M/q < 5 \) \( u/e \). In contrast, for the 100 keV Ar irradiations, the undersubtraction resulted in a higher background level which, for the ions presented in Table 2.1, was conservatively estimated to increase the uncertainty in the data to approximately twice the statistical error.

Three additional sources of variability in the data were results of using the naturally-occurring oxide surfaces of the targets. The first of these resulted from the inhomogeneity of the surface and, in particular, the inhomogeneity of residual contaminants such as Na. The second was a consequence of the change in the intensities of the various constituents during a measurement. Finally, the secondary electron emission was observed to change during bombardment. This affected the rate of sweeping through the mass range and resulted in different quantities of deposited charge/channel being collected. These errors were minimized by using samples which had been previously sputter etched using either 3 keV or 100 keV Ar\(^+\). As seen in Figures 2.26b and 2.27b, after sputter cleaning, the variability of the yields of the electronegative species was less than \(-25\%\) and of the metallic species was less than \(-10\%\) during a measurement. For the Al and Ni targets used during the 100 keV Ar\(^+\) irradiations, only 2-3 monolayers were removed prior to the measurements. As a result, the variabilities of the yields of the ions sputtered from these targets were larger during a measurement (These were approximately a factor of two for the F\(^+\) yield from Al and \(<25\%\) for the O\(^+\), Al\(^+\), and Al\(^{2+}\) intensities during the MeV ion irradiations (Figure 2.23). The variability of Ni\(^+\) emission was estimated to be \(~25\%\).) These variabilities would result in a serious
loss of precision for quantitative measurements. However, the results that are presented were not substantially limited by these uncertainties because the objective of the survey was to identify the qualitative differences in secondary ion emission that were most pronounced during 100 keV and 70 Mev ion irradiations of similarly-prepared surfaces.

It is interesting to note that if atomically-clean metallic surfaces had been prepared in vacuo, a potentially significant observation might have been missed. During one set of measurements, an Al foil was used that, in addition to the usual target preparation procedures described in Section 2.1, had been etched in a 10% NaOH solution for 30 seconds. This resulted in the emission of substantial numbers of Na+ secondary ions during MeV projectile bombardment while the emission of O+ ions was suppressed. Although the reduction of O+ emission may have been simply a geometric effect, i.e. fewer oxygen atoms on the surface, the measurements of Yu and Lang (Yu83) suggest an alternative explanation. For alkali atoms with ionization potentials (I) which were larger than the work function (φ) of a metallic or semiconductor surface, these workers observed that the yield of alkali secondary ions during 500 eV Ne+ ion bombardment decreased exponentially as the work function of the surface was lowered. Also, for atoms on surfaces with I < φ, secondary ion emission was constant as the work function was lowered until φ was slightly below I. At that point, the ion emission was observed to decrease exponentially for further decrements of φ. Yu and Lang interpreted these results as evidence for electron tunneling between the surface and the ejected atom which was enhanced as the work function decreased. For our measurements, the reduction in the work function of the surface due to the presence of Na may explain the reduction of O+ emission from this target during MeV ion irradiation. In an interesting avenue for future research, additional measurements under carefully controlled conditions are necessary to determine whether this hypothesis is correct.
The data presented above have demonstrated that 70 and 75 MeV projectiles are substantially more efficient than 100 keV projectiles in producing positive secondary ions from electronegative target constituents, especially $^{16}\text{O}^+$. The $\text{O}^+$ ions were often the most abundant species in the mass spectrum. In particular, there was an apparent lack of a strong dependence of emission of secondary ions on the ionization potential of the sputtered atom. This is in contrast to the general observation with keV projectiles that positive ion yields of different elements sputtered from a common matrix exhibit an inverse exponential dependence on the ionization potential of the emitted atom (Observation #1, Section 1.4).

In order to investigate these differences more fully and to determine if the yield of the electronegative species can be correlated with any obvious property of the primary ions, e.g. $\text{d}E/\text{d}x$, the variation of the yields of $^{16}\text{O}^+$, $^{19}\text{F}^+$, $^{51}\text{V}^+$, and $\text{VO}^+$ ions sputtered from a V target has been measured as a function of projectile energy. The experiment consisted of a series of measurements of positive secondary ion mass spectra using 10-90 MeV Br projectiles in 10 MeV steps. A vanadium target was chosen because it had been observed to emit $\text{O}^+$ ions intensely during MeV ion irradiation (Oc85a, Bi85a) and because data taken at three intermediate energies using a V target showed that the relative abundance of $\text{O}^+$ when compared with the principal metallic ion $\text{V}^+$ was strongly dependent on projectile energy (Bi85a). The mass spectrometer was set to sample secondary ions with energies up to 40 eV/q and the naturally-occurring oxide layers of the V target were studied in order to maintain consistency with these earlier results.

As noted above, the decision to use the naturally-occurring oxide surfaces introduced three sources of variability into the data. These variabilities were minimized by the following procedures. First, mass spectra were accumulated from a series of discrete locations on the target using identical 70 MeV $^{79}\text{Br}^{7+}$ irradiations. Subsequently, another spectrum was obtained at each location using primary ions at one energy in the 10-90 MeV range. Finally, measurements were repeated at each
Location using 70 MeV Br projectiles. In all of the irradiations, the total beam fluences at each location were held below $1.2 \times 10^{15}$/cm$^2$. Before and after each spectrum was accumulated, beam current measurements were made using a Faraday cup mounted on the target assembly to correct for changes in secondary electron emission during a measurement. Finally, the normalized intensity for each ion at each projectile energy was obtained as the ratio of the intensity of that ion to the average of the two 70 MeV Br irradiations made at the same location.

The results of the measurements are shown in Figure 2.16. In the figures, the normalized intensity of $^{16}$O$^+$, $^{19}$F$^+$, $^{51}$V$^+$, and VO$^+$ secondary ions are plotted as a function of projectile energy. The nuclear stopping cross section calculated on the basis of expressions given by Wilson et al. (Wi77b) has been superimposed on each figure with its magnitude given with reference to the axis on the right. The experimental errors presented result primarily from the uncertainty in beam current integration and from variation of the secondary ion emission as a function of target location and previous irradiation. Statistical errors were insignificant in all cases. Since for each ion the 70 MeV datum was obtained using three irradiations on the same spot (in the same way as the others), its value is near but not necessarily equal to 1.0.

Figure 2.16 shows that in the energy range 10-90 MeV, the increase in the intensity ratios $I(O^+)/I(V^+)$ and $I(F^+)/I(V^+)$ is a result of the decrease in the absolute intensity of V$^+$ emission. Also, the total yield of V$^+$ ions is, to a good approximation, proportional to the nuclear stopping cross section. This indicates that the yield of V$^+$ ions is proportional to the total sputtering yield provided that the yield of sputtered neutrals does follow $S_N(E)$. In addition, it may be inferred that the probability of ionization of a sputtered V particle is approximately constant in the energy range investigated. This differs significantly from the behavior that has been seen with 2-15 keV Ar projectiles (Wi75b) but is consistent with observations that have been reported for 150 keV ion bombardment of W (St72, St74) and for the emission of Al$^+$ and Cu$^+$ from targets bombarded by $^{252}$Cf fission fragments (Kn82).
Figures 2.16b and 2.16c show that the intensities of emission of O+ and F+ are essentially constant between 10 and 90 MeV. However, since the spectrum presented in Figure 2.14 for 100 keV Ar bombardment of V showed only a trace O+ signal and no detected F+ ions, there is a significant increase in the absolute yield of O+ and F+ ions with high velocity projectiles but this increase is most rapid for energies below 10 MeV. This agrees with the behavior reported by Becker et al. (Be83a) who, as noted above, have also studied secondary ion emission from metallic surfaces during MeV ion bombardment. For the targets and projectiles examined, they observed that the emission of non-metallic ions increased significantly in the range of projectile velocities from 0.2-0.7 cm/ns, while above this range the yields were approximately independent of projectile velocity. (The velocity of a 10 MeV Br ion is 0.5 cm/ns.)

The normalized intensity of VO+ emission is presented in Figure 2.16d. While it is also approximately independent of projectile energy, there is a tendency for it to decrease slowly. Such a decrease would be expected if the mechanism for production of these ions were the attachment of a V+ ion to a sputtered neutral O atom (or, in this case, the complementary process of attachment of an O+ ion to a neutral V atom) (Wi82a). However, given the relatively rapid decrease in V+ intensity and also of the expected yield of sputtered neutral V (assuming the neutral yield is proportional to $S_N(E)$), this mechanism cannot account for all of the VO+ intensity unless there is a substantial increase in desorption of neutral O which is not reflected in the ion yield.

The data presented in Figures 2.16a, b, and c clearly demonstrate that the V+ and O+ (and F+) secondary ions are produced by different mechanisms. Moreover, with these data, a significant constraint on possible theoretical models may be established. In the 10-90 MeV region, the electronic component of the stopping power, $S_E(E)$, of the Br ion increases by approximately a factor of three (No70, Zi80), yet the yield of O+ ions remains constant. If the underlying process which produces O+ ions is assumed to be at least proportional to $S_E(E)$, then these data require that a compensating phenomenon be present which effectively nullifies the increase in yield to be
derived from the larger $S_E(E)$ at higher ion energies. Since such a chance cancellation of effects is unlikely, we conclude that the emission of $O^+$ ions is not directly related to the total energy deposited in electronic excitation.

It is interesting to note, however, that for Br ions in the energy range studied, the primary ionization (calculated as in (F175)) varies much more slowly than the stopping power. The similarity of the behavior of $O^+$ ion emission is consistent with the speculation that for heavy ion bombardment a significant fraction of these ions may be being desorbed as a result of electronic transitions induced by fast secondary electrons, while $V^+$ ions are produced in collision cascades. This hypothesis is tested in the measurements described in Section 2.6.3 and the results are discussed in Chapter 5.

2.6 Energy Selection by a Commercial Electrostatic Energy Analyzer

2.6.1 Instrument and Procedure

Secondary ion mass spectra obtained using the voltage modulation technique demonstrated that this mode of ion energy selection was adequate for MeV projectiles. However, with keV projectiles, it did not sufficiently attenuate neutrals and high-energy secondary ions resulting in an unacceptably large background, especially at low masses (Figures 2.12-2.15). Since we wished to obtain a quantitative comparison of secondary ion intensities measured with keV and MeV primary ions, a commercial cylindrical mirror analyzer was installed as the energy pre-filter for the quadrupole mass analyzer (Figure 2.17).

Neutral particles, high-energy secondary ions, and backscattered primary ions were prevented from directly entering the mass filter by the energy analyzer's axial stop which had the same dimensions as the focus plate aperture. Secondary ions entered the analyzer through an annular grid surrounding the axial stop. By the proper choice of the cylindrical reflector potential
(V_1) and the potential of the central electrode (V_2), only ions within a selected energy range would pass through the analyzer. The focus plate was biased to optimize transmission of the system. In our measurements, a pass energy of approximately 5 eV with a 3 eV bandwidth (FWHM) was obtained with V_1=+2.00 V, V_2=-3.00 V, and the focus plate biased to -15.0 V. (For calibration measurements, see (Bl86).) In addition, since the central electrode was electrically connected to the axial stop and the annular grid, a small collection field was set up between the target and the energy analyzer.

The data acquisition was similar to that used during the 100 keV ⁴⁰Ar⁺ irradiations with two exceptions. First, since the secondary ions were energy analyzed prior to entering the quadrupole, only one mass spectrum was necessary to complete a measurement. Second, because of the short interval non-linearity of the Brookhaven current integrator (which is inherent in its design), it was replaced by a combination of a Keithley Model 410A picoammeter and a highly linear voltage-to-frequency converter. With this combination, it was possible to sweep more rapidly through a specified mass range.

2.6.2 Measurements

Two sets of measurements were performed with the mass filter coupled to the cylindrical mirror analyzer. First, the emission of positive secondary ions from Al, V, and Y surfaces was studied both as a function of deposited charge and projectile energy for 2.8-40 MeV ⁷⁹Br bombardment. During these measurements, the digital-to-analog converter (DAC) was programmed to repetitively step through four discrete voltage values. Each value determined a particular secondary ion to be examined. The analyzed ions were ¹⁶O⁺, ¹⁹F⁺, ⁵¹V⁺, and VO⁺ for the V target; ²⁷Al²⁺, O⁺, F⁺, and ²⁷Al⁺ for the Al target; and, O⁺, ³⁵Cl⁺, ⁸⁹Y⁺, and YO⁺ for the Y target. At each channel, only about 1 nC of charge was collected and the total accumulated charge
was ~2 μC for each ion studied. At each projectile energy, the intensity variations were measured from previously unirradiated samples with naturally-occurring oxide layers. Full mass spectra (mass range 1-150 u/e) were also obtained at each energy. In addition, during 20 MeV $^{79}$Br$^{5+}$ ion irradiations, intensity variations and full mass spectra were obtained from the Al and V targets both before and after sputter etching with 4 μA/cm$^2$ of 3 keV Ar for 1/2 hour.

Second, positive secondary ion mass spectra were measured from naturally-occurring oxide surfaces of Al and V targets bombarded by 50 and 100 keV $^{79}$Br$^{+}$ projectiles. Spectra were also obtained from the V target using 250 keV Br primary ions. Since the sputtering yields of the keV beams were large, a mass range of 1-75 u/e was used because it was our objective to use the minimum fluence of primary ions at each energy consistent with adequate statistics in the M$^+$ and MO$^+$ mass peaks (<7.5 x 10$^{12}$/cm$^2$).

### 2.6.3 Results

Typical mass spectra obtained from the V target bombarded by 40 MeV $^{79}$Br$^{5+}$ and 50 keV $^{79}$Br$^{+}$ projectiles are shown in Figures 2.18 and 2.19. Apart from the improved resolution and sensitivity, the spectra are very similar to the results presented in Section 2.5. A comparison of the figures clearly demonstrates the qualitative effects of increased projectile energy. In particular, the data show that O$^+$ secondary ion emission per projectile is approximately a factor of 100 greater for MeV ion bombardment. A substantial increase is also noted in F$^+$ ion emission. In addition, the decrease in the yield of V$^+$ secondary ions as the projectile energy increased was approximately equal to the diminution expected if the yield was proportional to $S_N(E)$ across the entire 50 keV to 40 MeV energy range.

The variation of the secondary ion yields obtained from the Al, V, and Y targets as a function of $^{79}$Br energy is presented in Figures 2.20-2.22. The nuclear stopping cross section, calculated
using the empirical formulae of Winterbon et al. (Wi70) has been superimposed on Figures 2.20a and 2.21a with its magnitude given with reference to the axes on the right. The minimum experimental errors reflect the 25% reproducibility obtained during a series of measurements of Al$^+$ and V$^+$ intensities during 100 keV $^{79}$Br$^+$ bombardment. The data obtained with the 2.8 MeV Br beam had significant uncertainties in beam current integration (~30%). Also, large statistical errors (up to 100%) were present for the O$^+$ and F$^+$ ion intensities during the keV ion irradiations because of the extremely low yields of these species at low beam energies.

These figures have a number of interesting features. First, although the agreement is poor, the intensities of Al$^+$ and V$^+$ secondary ions are approximately proportional to $S_N(E)$. These observations are consistent with the results for V$^+$ ion emission presented in Figure 2.16a and with the results obtained by Knippelberg et al. (Kn82) for Al$^+$ emission from targets bombarded by $^{252}$Cf fission fragments. Also, one may infer that the ionization probability of sputtered Al and V is approximately constant across the 50 keV to 40 MeV Br energy range provided that the total yield of sputtered particles is proportional to $S_N(E)$.

In contrast to the results for Al$^+$ and V$^+$, the yield of Y$^+$ secondary ions is approximately constant for 2.8-40 MeV Br bombardment. This is consistent with the results of Becker et al. (Be83a) for Y targets bombarded by $^{58}$Ni and $^{132}$Xe projectiles with velocities ranging from 0.2-1.4 cm/ns. Since these workers also observed that the Y$^+$ ion energy distribution extended to ~1 keV, the trend for Y$^+$ emission observed in Figure 2.22a indicates that the ionization probability of sputtered Y atoms varies as a function of projectile energy.

The variation of the yield of O$^+$ secondary ions from each of the targets is shown in part b of Figures 2.20-2.22. (Superimposed on Figure 2.21b are the primary ionization for Br in V and also the variation of the square of the effective charge ($Z_{eff}^2$) of Br projectiles in V as a function of the Br energy. The comparison of these curves with the O$^+$ data is discussed in Section 5.3.) Figures 2.20c and 2.21c show the change in F$^+$ emission from the Al and V targets, respectively. Figure
2.22c presents the variation of $^{35}$Cl+ emission from the Y target. In each case, there is a substantial increase in intensity as the energy of the projectile increases, especially below 20 MeV. These results are consistent with the data presented in Section 2.5 and also with the results of Becker et al. (Be83a). It is important to note that the uncertainties associated with the intensities of O+ and F+ obtained from the Al and V targets bombarded by 50 and 250 keV Br were sufficiently large so that the results were consistent with zero. The yields obtained for each species during 100 keV Br bombardment, however, are statistically significant.

The results for VO+ and YO+ secondary ion emission are presented in Figures 2.21d and 2.22d. For MeV bombarding energies, I(VO+) and I(YO+) decrease slowly with increasing projectile energy. The results for VO+ are consistent with the data presented in Figure 2.16d. A similar trend in the emission of YO+ has also been observed by Becker et al. (Be83a). The yields of VO+ secondary ions obtained during 50-250 keV Br bombardment were substantially higher than those obtained with MeV projectiles as would be expected if the mechanism for the production of the these ions were the attachment of a neutral O atom to a sputtered V+ ion (Wi82a). In Section 2.5.3.4, it was noted that the complementary process of the attachment of an O+ ion to a sputtered neutral V was also possible. The trend of O+ emission for the 2.8-20 MeV Br irradiations indicates that both these processes may be important in the formation of VO+ secondary ions. Since I(O+) increases rapidly in this energy range (Figure 2.21b), the trend of the combined ion yields (V+O→VO+ and V+O+→VO+) with beam energy would resemble the variation of I(VO+) (assuming that the O+ ion yield is proportional to the yield of neutral O). Above 20 MeV, the intensity of O+ emission was essentially constant so that I(VO+) again would be expected to be proportional to $S_N(E)$. The results presented in Figure 2.16d show that this behavior is observed to a good approximation.

The variation of the yield of Al2+ secondary ions with Br energy is shown in Figure 2.20d. For the keV irradiations, no statistically significant Al2+ signal was observed. At these energies, the tails
of the mass peaks at 13 and 14 u/e limited the sensitivity of the measurements to $>1 \times 10^{-8}$ counts/ projectile. The negligible yield is consistent with previous measurements from oxidized Al surfaces using keV projectiles where intensity ratios $I(Al^{2+})/I(Al^+)$ as low as 0.01% have been observed. In our measurements, the lowest observable ratio with keV projectiles was ~0.1%. In contrast to these observations, a substantial number of Al$^{2+}$ ions were seen with MeV projectiles. Also, the yield was approximately independent of projectile energy. The latter observation is consistent with the results of Knippelberg et al. (Kn82) who observed a slow decrease in Al$^{2+}$ emission from sputter-etched Al bombarded by $^{252}$Cf fission fragments.

In Section 2.5.3.2, it was postulated that the same mechanism which enhances O$^+$ emission during MeV ion bombardment may also be responsible for the enhanced emission of Al$^{2+}$ secondary ions. The data of Figures 2.20b and 2.20d, however, do not support such an inference since the dependence of the yields of the two species as a function of Br energy are substantially different. Also, Becker et al. (Be83a) have observed that the energy distributions of the Al$^{2+}$ ions emitted during $^{58}$Ni, $^{132}$Xe, and $^{238}$U bombardment have slowly decreasing high energy tails which extend up to several hundred eV. In contrast, the O$^+$ secondary ions have energies of only a few eV (Section 2.5.3.2). Moreover, Wien and Becker have observed that the yield of Al$^{2+}$ ions emitted from an Al target during bombardment by $^{252}$Cf fission fragments was independent of the exposure of the surface to oxygen (Wi83). These data indicate that the emission of multicharged Al ions is a result of direct impacts with the projectile or fast recoil atoms. In contrast, the results for O$^+$ emission (and for the other non-metallic secondary ions) indicate that these ions are generated as a result of electronic excitation.

As noted previously, the emission of positive secondary ions from Al, V, and Y during MeV ion irradiations was studied both as a function of projectile energy and as a function of deposited charge. The dose studies were performed to obtain a quantitative understanding of the variation of secondary ion emission during a measurement. Figures 2.23-2.25 present the results obtained for each target as a function of collected charge for 3.4 and 30 MeV Br bombardments. Figures 2.26
and 2.27 present results obtained from Al and V bombarded by 20 MeV Br projectiles both before and after sputter etching with 3 keV Ar at ~4μA/cm² for 1/2 hour.

These data demonstrate that, for previously unirradiated targets, the emission of positive secondary ions from the electronegative surface constituents varied by up to a factor of three during a measurement. It is interesting to note that, because of the thick oxide layer, O⁺ emission from the Al sample varied by only about 10% during a measurement (following the initial increase). In comparison, the rapid variation of F⁺ from Al shows that these constituents are concentrated on the surface of the sample. The yields of the metallic and metallic oxide species varied slowly as a function of deposited charge. In all cases, apart from the first few nC of collected charge, these species varied by less than approximately 25% during a measurement.

In addition, these results demonstrate that the secondary ion emission as a function of deposited charge is also a function of the projectile energy. In particular, it is interesting to note that for 3.4 MeV Br bombardment, there is a relatively slow increase in emission from the electronegative surface constituents from the time the beam was first incident on the targets while this increase is quite rapid, although not instantaneous, for the 30 MeV Br irradiations. The data at the other beam energies show that there is a smooth transition from a slow rise to a rapid rise as the energy of the projectile increases.

The emission of metallic and metallic oxide secondary ions as a function of beam dose also changed as the projectile energy increased. For the 30 MeV Br irradiations, strong M⁺ and MO⁺ intensities were observed for the first few nC of collected charge. The signal then rapidly dropped to a significantly lower level and, subsequently, changed very slowly with accumulated charge. For the 3.4 MeV Br irradiations, only the YO⁺ signal exhibited this behavior. A smooth increase in the appearance of this trend for the M⁺ and MO⁺ ions was also observed as the projectile energy increased.

Figures 2.28 and 2.29 show that secondary ion intensities from a sputter-etched target vary very slowly as a function of beam dose. Unlike the previously-unirradiated samples, the intensities
of the electronegative constituents immediately reached their maximum values upon bombardment. Also, the behavior observed in the first few nC of collected charge for the metallic and metallic oxide ions has disappeared after sputter cleaning.

Since the observations presented in Figures 2.23-2.27 show that the emission of secondary ions of the various surface constituents changes during MeV ion bombardment, future measurements of secondary ion emission during MeV ion irradiations should use surfaces which have been prepared and characterized in vacuo. Also, the observed trends of ion emission as a function of deposited charge indicate that measurements of these effects under carefully controlled conditions are an interesting avenue for future research.
Table 2.1 Relative intensities of metal, oxygen, and metal oxide ions derived from the data of Figures 2.12-2.15 (See Section 2.5.3.2). The data for each target are normalized to $M^+=100$ with the Ar and Br data individually normalized. The quoted errors are statistical.
<table>
<thead>
<tr>
<th></th>
<th>Al⁺</th>
<th>Al²⁺</th>
<th>Al³⁺</th>
<th>O⁺</th>
<th>O²⁺</th>
<th>AlO⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁰Ar</td>
<td>100</td>
<td>&lt;2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>⁷⁹Br</td>
<td>100</td>
<td>20.5±0.4</td>
<td>1.5±0.2</td>
<td>87±1</td>
<td>1.4±0.2</td>
<td>2.4±0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ti⁺</th>
<th>O⁺</th>
<th>TiO⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁰Ar</td>
<td>100</td>
<td>-</td>
<td>9.7±0.2</td>
</tr>
<tr>
<td>⁷⁹Br</td>
<td>100</td>
<td>384±7</td>
<td>22.6±0.8</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th></th>
<th>V⁺</th>
<th>V₂⁺</th>
<th>O⁺</th>
<th>VO⁺</th>
<th>V₂O⁺</th>
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<tbody>
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<td>⁴⁰Ar</td>
<td>100</td>
<td>3.3±0.1</td>
<td>2.2±0.3</td>
<td>7.4±0.1</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>⁷⁹Br</td>
<td>100</td>
<td>0.9±0.2</td>
<td>92±2</td>
<td>9.2±0.4</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ni⁺</th>
<th>O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁰Ar</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>⁷⁹Br</td>
<td>100</td>
<td>47±3</td>
</tr>
</tbody>
</table>
Figure 2.1 Schematic diagram of the differentially-pumped ultra-high vacuum (UHV) beam line attached to the R30 beam line of the Yale MP-1 tandem Van de Graaff accelerator.
Figure 2.2 Schematic diagram of the differentially-pumped UHV beam line connected to the 300 kV Cockcroft-Walton accelerator.
Figure 2.3 (a) Schematic diagram of a quadrupole mass analyzer. (b) Schematic diagram showing three stable trajectories of a particle through a quadrupole mass filter. (From (Da76a))
Figure 2.4 Relative transmission of the UTI 100C quadrupole mass filter as a function of the mass of the analyzed ion. (Uthe Technology Inc., 100C Manual)
Figure 2.5 Experimental geometry used during the preliminary measurements of secondary ion mass spectra. The quadrupole mass spectrometer was positioned at an angle of 75° with respect to the incident 75 MeV $^{79}$Br$^{8+}$ ion beam. The target was positioned at an angle of 45° with respect to the incident beam.
Figure 2.6 Schematic diagram of the quadrupole mass spectrometer with the improved voltage modulation energy pre-filter. The spectrometer was aligned along the target's surface normal, which was at an angle of 30° with respect to the MeV ion beams and at an angle of 45° with respect to the keV projectiles.
QUADRUPOLE MASS SPECTROMETER
Figure 2.7 Schematic diagram of the electronics used for measurements of secondary ion mass spectra obtained with the voltage modulation energy pre-filter during MeV ion irradiations.
Figure 2.8 Schematic diagram of the electronics used for measurements of secondary ion mass spectra obtained with the voltage modulation energy pre-filter during keV ion irradiations.
Figure 2.9 Secondary ion mass spectra obtained from a Cu target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions (a) prior to sputter cleaning and (b) after sputter cleaning with 3 kev $^{40}$Ar$^+$ ions. In Figures 2.9-2.11, the energy range of ions entering the quadrupole is (0-10)$q$ eV, where $q$ is the ion charge.
75 MeV $^{79}\text{Br}^{8+} \rightarrow \text{Cu}$

(3 keV Ar Pre-sputtered)
Figure 2.10 Secondary ion mass spectra obtained from a Nb target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions (a) prior to sputter cleaning and (b) after sputter cleaning.
75 MeV $^{79}\text{Br}^{8+}$ - Nb
(3 keV Ar Pre-sputtered)
Figure 2.11 Secondary ion mass spectra obtained from a Ta target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions (a) prior to sputter cleaning and (b) after sputter cleaning.
75 MeV $^{79}$Br$^{8+}$ → Ta
(3 keV Ar Pre-sputtered)
Figure 2.12 Secondary ion mass spectra obtained from an Al target during 70 MeV $^{79}$Br$^{7+}$ and 100 keV $^{40}$Ar$^{+}$ ion bombardment. In Figures 2.12-2.16, the energy range of ions entering the quadrupole is (0.1-40)q eV, where q is the ion charge.
Figure 2.13 Secondary ion mass spectra obtained from a Ti target during 70 MeV $^{79}\text{Br}^7+$ and 100 keV $^{40}\text{Ar}^+$ ion bombardment.
COUNTS (arbitrary units)

-  

70 MeV 79Br^7+ → Ti

100 keV 40Ar^+ → Ti

b/μ

10 20 30 40 50 60 70

Na^+ K^+ TiO^+ Ti^+ O^+ H^+
Figure 2.14 Secondary ion mass spectra obtained from a V target during 70 MeV $^{79}$Br$^7+$ and 100 keV $^{40}$Ar$^+$ ion bombardment.
Figure 2.15 Secondary ion mass spectra obtained from a Ni target during 70 MeV $^{79}\text{Br}^7+$ and 100 keV $^{40}\text{Ar}^+$ ion bombardments.
COUNTS (arbitrary units)

70 MeV $^{79}\text{Br}^7$ $\rightarrow$ Ni

100 keV $^{40}\text{Ar}^+$ $\rightarrow$ Ni

COUNTS (arbitrary units)

$H^+$

$O^+$

$Na^+$

$Ni^+$

$Ni^+$

$m/q$

$m/q$
Figure 2.16 The variation of yields (normalized as discussed in Section 2.5.3.4) of (a) V+, (b) O+, (c) F+, and (d) VO+ secondary ions as a function of 10-90 MeV $^{79}$Br projectile energy. Superimposed on each figure is the nuclear stopping cross section for Br ions incident on V with its magnitude in reference to the axis on the right.
Normalized Intensity vs. Beam Energy (MeV)

- 79Br → V
- V⁺ Secondary Ion Intensity
- Nuclear Stopping Cross Section

Normalized Intensity

Beam Energy (MeV)

S_{N}(E) (eV·cm²/10^{15} ATOMS)
Normalized Intensity

**Normalized Intensity**

\[ S_{N}(E) \text{ (eV cm}^{-2} \text{cm}^{-2}/10^{15} \text{ atoms}) \]

**O\(^{+}\) Secondary Ion Intensity**

**Nuclear Stopping Cross Section**

\[ 79_{\text{Br}} \rightarrow V \]

**Beam Energy (MeV)**
$^{79}\text{Br} \rightarrow \text{V}$

- $F^+$ Secondary Ion Intensity
- Nuclear Stopping Cross Section

** normalized intensity vs. beam energy (MeV) **

$S_N(E)$ (eV·cm$^2$/10$^5$ ATOMS)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0

0 10 20 30 40 50

0 20 40 60 80 100

beam energy (MeV)
$79\text{Br} \rightarrow \text{V}$

- VO$^+$ Secondary Ion Intensity
- Nuclear Stopping Cross Section

**Normalized Intensity** vs **Beam Energy (MeV)**

- $S_N(E)$ (eV cm$^2$/10$^5$ Atoms)
Figure 2.17 A schematic diagram of the quadrupole mass spectrometer with a commercial cylindrical mirror analyzer (Kratos Analytical, Inc.) as the energy pre-filter. The spectrometer was aligned along the target's surface normal, which was at an angle of 30° with respect to the incident beam for the MeV ion irradiations and at an angle of 45° for the keV ion irradiations.
Figure 2.18 Positive secondary ion mass spectra obtained from a V target under 40 MeV $^{79}$Br$^{5+}$ ion bombardment. In Figures 2.18-2.27, the cylindrical mirror energy analyzer was adjusted to pass 5 eV secondary ions with a bandwidth of 3 eV (FWHM).
Figure 2.19 Positive secondary ion mass spectrum obtained from a V target under 50 keV $^{79}$Br$^+$ ion bombardment.
Figure 2.20 The variation of the positive secondary ion yields of (a) Al+, (b) O+, (c) F+, and (d) Al^{2+} as a function of 50 keV to 40 MeV ^{79}\text{Br} projectile energy. Superimposed on part (a) is the nuclear stopping cross section for Br in Al with its magnitude given in reference to the axis on the right.
Figure 2.21 The variation of the positive secondary ion yields of (a) V⁺, (b) O⁺, (c) F⁺, and (d) VO⁺ as a function of 50 keV to 40 MeV ⁷⁹Br projectile energy. Superimposed on part (a) is the nuclear stopping cross section for Br in V with its magnitude in reference to the axis on the right. Superimposed on part (b) are the primary ionization for Br in V (as calculated in (FI75)) (dotted curve) and also the variation of $Z_{\text{eff}}^2$ (He60) (solid curve).
Figure 2.22 The variation of the positive secondary ion yields of (a) $Y^+$, (b) $O^+$, (c) $Cl^+$, and (d) $YO^+$ as a function of 2.8-40 MeV $^{79}$Br projectile energy.
Figure 2.23 The variation of the positive secondary ion yields of (a) Al⁺, (b) O⁺, (c) F⁺, and (d) Al²⁺ as a function of deposited charge for (A) 3.4 MeV $^{79}$Br²⁺ and (B) 30 MeV $^{79}$Br⁵⁺ ion bombardment of Al. For Figures 2.23-2.27, each channel corresponds to approximately 1 nC of collected charge.
COUNTS/INCIDENT ION ($10^7$)

CHANNEL NUMBER

0 3 6 9 12

500

1000

1500

2000

CHANNEL NUMBER

3.4 MeV

$^{79}$Br$^{2+}$-Al

A$^{2+}$ YIELD

F$^+$ YIELD

O$^+$ YIELD

Al$^+$ YIELD

(a)
30 MeV $^{79}$Br$^{5+}$ → Al

$\text{Al}^+ \text{ YIELD}$

$\text{O}^+ \text{ YIELD}$

$\text{F}^+ \text{ YIELD}$

$\text{Al}^{2+} \text{ YIELD}$
Figure 2.24 The variation of the positive secondary ion yields of (a) V+, (b) O+, (c) F+, and (d) VO+ as a function of deposited charge for (A) 3.4 MeV $^{79}$Br$^{2+}$ and (B) 30 MeV $^{79}$Br$^{5+}$ ion bombardment.
Graph (A) shows the yields of different ions from a 3.4 MeV $^{79}\text{Br}^{2+}$ beam incident on a target. The yields are measured as counts per incident ion and plotted against channel number.

- (a) $V$ ion yield
- (b) $O^+$ ion yield
- (c) $F^+$ ion yield
- (d) $\text{VO}^+$ ion yield
30 MeV $^{79}\text{Br}^{5+} - \text{V}$

(a) $V^+$ YIELD

(b) $O^+$ YIELD

(c) $F^+$ YIELD

(d) $V^0^+$ YIELD

COUNTS / INCIDENT ION ($10^7$)

CHANNEL NUMBER
Figure 2.25 The variation of the positive secondary ion yields of (a) Y⁺, (b) O⁺, (c) Cl⁺, and (d) YO⁺ as a function of deposited charge for (A) 3.4 MeV $^{79}$Br²⁺ and (B) 30 MeV $^{79}$Br⁵⁺ ion bombardment.
30 MeV $^7_9\text{Br}$, $^5_9\text{Br}$ $\rightarrow \gamma$

Y$^+$ YIELD

0$^+$ YIELD

C$^+$ YIELD

Y$^0$ YIELD

CHANNEL NUMBER

COUNTS/INCIDENT ION (10$^7$)

(a)

(b)

(c)

(d)
Figure 2.26 The variation as a function of deposited charge of the positive secondary ion yields of (a) Al$^+$, (b) O$^+$, (c) F$^+$, and (d) Al$^{2+}$ emitted from an Al target bombarded by 20 MeV $^{79}$Br$^{4+}$ ions (A) prior to and (B) after sputter cleaning with 3 keV $^{40}$Ar$^+$. 
(A) 10

20 MeV $^{79}\text{Br}^4+$ – Al
$\text{Al}^+$ YIELD

COUNTS/INCIDENT ION ($10^7$)

CHANNEL NUMBER
20 MeV $^{79}$Br$^{4+}$→Al
Al$^+$ YIELD
(3 keV Ar Sputter Etched)
Figure 2.27 The variation as a function of deposited charge of the positive secondary ion yields of (a) V⁺, (b) O⁺, (c) F⁺, and (d) VO⁺ emitted from a V target (A) prior to and (B) after sputter cleaning.
20 MeV $^{79}\text{Br}^{4+} \rightarrow V$

V$^+$ YIELD

O$^+$ YIELD

F$^+$ YIELD

V O$^+$ YIELD

CHANNEL NUMBER

COUNTS/INCIDENT ION ($10^7$)
20 MeV $^{79}$Br$^{4+}$-V

V$^+$ Yield

(3 keV Ar Sputter Etched)

(B)

COUNTS/INCIDENT ION (10$^7$)

CHANNEL NUMBER

(b)

O$^+$ YIELD

(c)

F$^+$ YIELD

(d)

V0$^+$ YIELD
CHAPTER 3
SECONDARY ION ENERGY SPECTROMETRY

As noted briefly in Section 1.2, neutral atom energy spectra have been useful in distinguishing between sputtering mechanisms. Thompson (Th68) and Weller (We78) demonstrated that a collisional description of the sputtering process was consistent with the energy spectra measured during keV ion bombardment of Au and U, respectively. In particular, the predicted $E^{-2}$ dependence of the high energy tails of the distributions (Th68, Si69) were reproduced reasonably well in the experiments. In contrast, during MeV ion bombardment of UF$_4$, a dielectric material, Griffith (Gr79) measured energy spectra that decreased asymptotically as $E^{-5}$. These different features of the energy spectra demonstrated that different sputtering mechanisms were dominant in the experiments. (We note that Griffith also measured sputtering yields that were two to three orders of magnitude larger than those predicted by eq. (1.1) and that the yields were related to the electronic energy loss of the projectile in the target (Gr79)).

Secondary ion energy distributions, while more straightforward to measure than neutral atom spectra, are more difficult to interpret because of the uncertainty in the secondary ion emission mechanisms (Section 1.4). However, for keV projectile bombardment of metallic surfaces, secondary ion energy distributions are generally observed to peak at low energies (5-10 eV) and they have slowly decreasing high energy tails which may extend up to a keV (Observation #3, Section 1.4). Significant deviations from these observations in secondary ion energy spectra measured during MeV heavy ion bombardment of metallic surfaces would indicate that different ionization or sputtering mechanisms were dominant in the two energy regimes. In addition, such findings would be consistent with the mass spectrometric measurements presented in Chapter 2.

In this chapter, a measurement of secondary ion energy spectra from Cu, Nb, and Ta foils during 75 MeV $^{79}$Br$^{8+}$ bombardment is presented. The results are compared with the general observation for keV projectiles and are discussed with respect to the mass spectrometric data.
presented above. First, the electrostatic energy analyzer and the procedure used during the measurement are discussed in detail.

3.1 The Spectrometer

The spectrometer was a doubly-focusing spherical electrostatic energy analyzer that was designed following the work of Siegbahn et al. (Si67). These workers constructed a large spectrometer with inner and outer sector radii of 32 and 40 cm, respectively, for use in electron spectroscopy. Since we wanted a compact analyzer, we chose radii of 3.25 and 4.05 cm. The completed spectrometer is shown in cross section in Figure 3.1 and as used during the measurements in Figure 3.2. The electrodes, which were 160° spherical sectors, were made of OFHC copper. They were also electroplated with silver and gold to help eliminate charge buildup on the electrodes which would result in patch potentials. The retainer segments and entry plates were 304 stainless steel and also were electroplated with gold. Electrical insulation between the electrodes and the retainer segments was provided by 1/8" sapphire beads. The beads were seated in hemispherical pockets in each piece resulting in a 1 mm distance between the electrodes and the retainer segments. Structural support was obtained by bolting the entry plates into the endpieces of the retainer segments. The pressure generated by the segments on the sapphire beads was sufficient to hold the spherical electrodes firmly in place.

The entrance structure of the analyzer, shown in detail in Figure 3.2, consisted of a stainless steel collimator 2 cm long with a 1 mm opening, two mesh grids, and machinable glass ceramic insulators. The grids were 200 lines/inch Ni mesh sandwiched between Ta disks that were spot-welded together with either 1 or 2 mm apertures. The first grid (1 mm aperture) was connected electrically to the collimator and was the defining aperture for entering secondary ions. The solid angle subtended by this aperture was 0.7 m sr. The second grid was connected to the entry plate opening and formed an acceleration plane. The center line of the collimator was situated on the
zero potential line of the analyzer corresponding to a radius of 3.61 cm.

3.2 Operation

The geometry for secondary ion energy distribution measurements is shown in Figure 3.2. Particles sputtered from the target by the 75 MeV $^{79}$Br$^{8+}$ beam passed through a nominally field-free region to enter the collimator which was maintained at ground potential. At this point, two modes of operation could be used for analysis of the secondary ions: sector field sweeping and constant transmission energy.

For sector field sweeping, equal and opposite ramp voltages were applied to the spherical electrodes. The entry plates, Ni mesh grids, and support structure remained at ground potential. Since the pass energy of the analyzer is proportional to the potential difference, $\Delta V$, of the electrodes (Section 3.4.1), the changing $\Delta V$ caused the input distribution of particles to be analyzed. With this mode of operation, the efficiency of transmission and energy resolution will change as $\Delta V$ increases. As a result, sector field sweeping was only used during testing of the analyzer (Section 3.4.2).

For the measurements, we wished to maintain uniform energy resolution and transmission efficiency. Therefore, we used the constant transmission energy mode of operation. In this case, the potential difference between the electrodes is kept constant. In the measurements presented below, a value of $\Delta V=19.10$ V was used which resulted in a pass energy of 44.50 eV (Section 3.4.2). After passing through the grounded collimator and the first grid, the ions were accelerated by a potential, $V_a$, applied to the second grid. This voltage was the average value of the analyzer electrodes (Figure 3.3). Particles of appropriate energy passed through the analyzer and a 1 mm aperture at the exit and were detected by a channel electron multiplier operating in pulse counting mode (Galileo Electro-Optics Inc., Model 4039). By sweeping the potential of the second grid
through a selected range, the input distribution of secondary ions was analyzed. It is noted that during the measurements the secondary ions were always accelerated to a higher energy. As a result, the ion trajectories were refracted toward the normal of the plane of the second grid, thereby enhancing the transmission of the system.

3.3 Data Acquisition

Similar to the mass spectrometric measurements, the data acquisition was a two step process: processing the channeltron signals and controlling the analyzer voltages to sweep through a selected ion energy range. Figure 3.3 shows a schematic diagram of the electronics used during constant transmission energy measurements. The channeltron signals were pre-amplified, amplified, converted into a logic signal, and counted in a scaler. Beam current from the target, measured without secondary electron suppression, was digitized by the Brookhaven integrator and counted in a second scaler. These scalers were interfaced to the IBM 4341 computer by the Front End (Nu67). The Data Acquisition Language was used to create a multichannel scaler for storage of the ion energy spectra.

At the start of a measurement, the ramp voltage of the second grid, which was generated by an Ortec 487 Spectrum Scanner and a directly-coupled linear amplifier, was set to its initial value. After a fixed amount of collected charge, a logic signal from the beam current scaler would be generated. This signal had two purposes. First, it would trigger the ramp voltage to step to its next value. Second, the pulse would serve as an event trigger and would be sent to a special input of the Front End to send an instruction to the computer to read the two scalers, store the data in the multichannel scaler, and advance the channel of the scaler. Spectra were produced by sweeping the average voltage of the analyzer through a range of 40.4 V.
3.4 Analysis of the Spectrometer

3.4.1 Theoretical Analysis

The electric field of an analyzer with spherical electrodes is described by Laplace's equation:

\[ \frac{1}{r} \frac{d^2}{dr^2} (r \Phi) + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Phi}{d\theta}) + \frac{1}{(r^2 \sin^2 \theta)} \frac{\partial^2 \Phi}{\partial \Phi^2} = 0 \]  

(3.1)

where \( \Phi(r, \theta, \phi) \) is the potential at any point between the electrodes. In the first approximation, we may consider an ideal analyzer where \( \Phi \) is independent of \( \theta \) and \( \phi \). In that case, Laplace's equation may be written as:

\[ \frac{1}{r} \frac{d^2}{dr^2} (r \Phi) = 0. \]  

(3.2)

With the boundary conditions that \( \Phi(r_1) = -V \) and \( \Phi(r_2) = +V \), where \( r_1 = 3.25 \text{ cm} \) is the inner electrode radius and \( r_2 = 4.05 \text{ cm} \) is the outer electrode radius, equation (3.2) may be solved to find \( \Phi(r) \):

\[ \Phi(r) = V[(r_1+r_2)/(r_2-r_1) + (2r_1r_2/(r_1-r_2))/r]. \]  

(3.3)

The entrance radius was chosen on the zero potential line which corresponds to \( 3.61 \text{ cm} \). The relationship between the electrode voltages and the energy of the particle traversing the nominal (central) trajectory may be determined to be:
where $q$ is the ion charge and $\Delta V=2V$. The quoted uncertainties are the result of small misalignments ($<0.003^\circ$) that were unavoidable during assembly of the analyzer.

A more detailed study of particle trajectories through the spectrometer must be made to determine its resolution. A number of workers (Pu38, Ro51, Ew55, Bi60, Ri60, Hu64, Wo67) have presented the basic theory of spherical electrostatic prisms. Ewald and Liebl (Ew55), in particular, have computed the radial and axial orbit equations for particles in the vicinity of the nominal trajectory, i.e. circular orbit, to second order in angle and position. Using their formalism, we calculated the orbit equations for our analyzer and developed a Monte Carlo computer simulation to model the motion of secondary ions from the target to the detector. In a sample calculation, ions of 50 eV were used and the pass energy was swept from 49.0 to 51.0 eV. The results are shown in Figure 3.4 and indicate a fractional resolution of 1.28%.

### 3.4.2 Experimental Calibration

A measurement was also performed to determine the pass energy-potential difference proportionality constant and the energy resolution of the analyzer. In this experiment, an indirectly-heated Cs ion source (Spectra-Mat Inc., Model 600) was used to obtain Cs$^+$ ion beams of varying energies which were incident upon the entrance structure of the analyzer. Using both the sector sweeping and constant transmission energy modes, a series of energy spectra were obtained for 1 eV to 500 eV Cs$^+$ ions. Sample spectra measured using the two modes are shown in Figure 3.5. Using the centroids of the peaks, the potential difference of the electrodes was determined as a function of Cs$^+$ ion energy (Figure 3.6). The slope of the line, which is the $E-\Delta V$ proportionality constant, was determined by a least-squares fit to the data to be $2.330\pm0.005$ in good agreement with the value of $2.281\pm0.045$ from eq. (3.5). In Figure 3.7, the FWHM of the

$$E = (2.281\pm0.045) q\Delta V \quad \text{(3.4)}$$
peaks, $\Delta E$, are plotted versus the Cs ion energy. The slope of the line, which in this case is the fractional resolution of the analyzer, was found by a least-squares fit to be $1.15 \pm 0.01\%$. This result, which is better than the $1.28\%$ obtained during the Monte Carlo simulation, was lowered by the small collection field set up between the ion source and the collimator which refracted the trajectories of the Cs ions toward the normal of the plane of the second grid to enhance the transmission of the system.

It is important to note two additional points regarding Figures 3.6 and 3.7. In each case, the y-intercept of the straight-line fit to the data does not pass through the origin. The small negative value observed in the $E-\Delta V$ plot was a consequence of contact potentials in the system. During the calibration measurement, several different power supplies were used to bias the ion source and the analyzer electrodes. The value of the slope did not change for the various supplies but the intercept varied from $-0.83$ eV to $2.43$ eV. The contact potentials were a source of error during the measurements discussed below. The y-intercept of the $\Delta E$ vs. $E$ plot is a measure of the intrinsic energy width of the Cs ion source. The value of $0.14 \pm 0.01$ eV corresponds to a Maxwellian energy distribution of approximately 900 °K which is in reasonable agreement with the specifications of the manufacturer (Spectra-Mat, Inc.).

### 3.5 Measurements and Results

Positive secondary ion energy spectra were obtained from Cu, Nb, and Ta targets bombarded by 75 MeV $^{79}$Br$^8+$ projectiles. As noted in Section 3.2, the constant transmission energy mode of the spectrometer was used during the measurements. Preliminary results, however, demonstrated that an artifact was present in the spectra which was related to the potential, $V_a$, applied to the second grid of the entrance structure. This signal peaked at $V_a \approx 0$ with a sharp cutoff for $V_a > 0$ and a relatively slow cutoff for $V_a < 0$. The magnitude of the signal was approximately
equal for each target and also approximately independent of the potential difference, $\Delta V$, of the spherical electrodes. In addition, the artifact was not present during testing of the spectrometer with the Cs ion source (Figure 3.5). Although the cause of the anomalous signal is not known with certainty, its absence during testing indicates that it is probably related to either the large number of secondary electrons (~$2 \times 10^8$/s) or sputtered neutral particles entering the collimator during bombardment. In order to reduce the effects of this signal upon the energy spectra, $V_a$ was swept from -47.6 V to -7.4 V. The tail of the signal was taken into account by measuring spectra for each target with $\Delta V=19.10$ V and $\Delta V=0$ V. By subtracting the spectrum obtained when $\Delta V=0$ from that obtained when $\Delta V=19.10$ V, the anomalous signal was effectively eliminated.

Energy spectra were measured from the Cu, Nb, and Ta targets both before and after 1/2 hour of sputter cleaning using 3 keV Ar$^+$ at a current density of ~3 $\mu$A/cm$^2$. It is important to note the previous irradiation history of the targets. The Nb and Ta targets had been sputter etched to remove approximately 100 monolayers of material and exposed to 50 L of residual gas prior to the measurements. The Cu target had been sputter cleaned to remove 300 monolayers of material, exposed to 30 L of residual gas, sputter etched to remove an additional 50 monolayers, and exposed to 3 L of gas prior to the measurement. Thus, the Nb and Ta targets had irradiation histories similar to the targets used during the preliminary mass spectrometric measurements (Figures 2.10 and 2.11). The Cu target, on the other hand, had been irradiated extensively and, as a result, the "dirty" target differs from the sputter etched target only by a thin layer of adsorbed residual gas.

The total integrated ion energy spectra obtained before and after sputter cleaning are presented in Figures 3.8-3.10. The two curves in each figure have been normalized to the same number of incident Br projectiles. Because of the uncertainty in locating the zero of energy due to the presence of contact potentials (Section 3.4.2), the spectra have been plotted as a function of channel number. The energy calibration for each figure is 0.039 eV/channel. The location of zero energy at channel 76 is probably accurate to about 1 eV. (The positions of $E=0$ and $E=10$ eV are
noted by vertical arrows in each figure.) For each target, the reduction in ion yield resulting from sputter etching is approximately consistent with that expected on the basis of the mass spectra presented in Figures 2.9-2.11. Thus, for Cu and Nb, significant reductions in the ion yields are seen, while for Ta only a small change is observed.

The location of the most probable energy in these spectra at approximately 2 eV argues against a thermal emission process as observed in some dielectric targets (Gr79). This would be consistent with the mass spectrometric data for the atomic metal ions presented in Chapter 2 which indicated that these ions were produced by collisional processes. However, the decrease in ion yields above the most probable energy is more rapid than the $E^{-2}$ dependence generally observed for neutral metal atoms (Th68) and is much more rapid than for atomic ions sputtered by keV ion beams (Observation #3, Section 1.4). In fact, virtually all ions that we observed have energies below 20 eV. The fact that a substantial fraction of the secondary ions were surface contaminants (Figures 2.9-2.11), that these ions were observed to have very low energies (Section 2.5.3.2), and, that a number of atomic metal ions have energies above 40 eV (Section 2.5.3.2) demonstrates that the energy spectra presented in Figures 3.8-3.10 must be dominated by contaminant ions. (The majority of ions in the spectrum obtained from sputter cleaned Cu must be low energy hydrogen ions desorbed from the surface.)

This conclusion is supported by the results of Becker et al. (Be83a) who, as discussed in Chapter 2, have also studied secondary ion emission from sputter-cleaned metallic surfaces during MeV heavy ion bombardment. For Ta irradiated by $^{132}\text{Xe}$ projectiles at a velocity of 1.25 cm/ns, these workers observed comparable numbers of Ta+, O+, and C+ secondary ions and a very large number of H+ ions ($I(H+)-50 I(M+)$). The metal ions produced broad peaks in the time-of-flight spectrum which implied that the energy distribution of these ions had high-energy tails which extended out to about 1 keV. In contrast, the contaminant ions generated narrow peaks in the spectrum which indicated that these ions had energies of only a few eV.

It is also interesting to compare the spectra presented in Figures 3.8-3.10 with the results
obtained by Williams during 2-10 keV Ar+ and O2+ and 14.5 keV electron bombardment of fluorinated Si and chlorinated Al (Wi81, Section 1.4.3). As shown in Figure 1.6, the energy distribution of the F+ secondary ions produced during ion bombardment was similar to that generated during electron irradiation. The distribution peaked at ~2-3 eV and virtually all the F+ ions had energies below 20 eV. In contrast, the 30Si+ energy distribution decreased slowly as the ion energy increased. Williams has postulated that the F+ ions were produced as a result of electron-stimulated desorption (ESD) induced by collisionally-produced silicon LVV Auger electrons. The energy spectra that are presented in Figures 3.8-3.10 are similar to the distributions of F+ ions presented in Figure 1.6. This observation, as well as the applicability of Williams' model of ion formation to our data, is discussed further in Section 5.3.

3.6 Analysis of Uncertainties

Three primary sources of uncertainty were present in the measurements of the energy spectra shown in Figures 3.8-3.10. First, in the mode in which it was used, the energy analyzer was not capable of mass differentiation. Second, the use of a background subtraction to eliminate the artifact in the ion energy spectra resulted in large relative errors when the two signals were of comparable size. In the energy range presented in the figures, this uncertainty was below ~10% in each case except for the sputter-etched Cu sample where statistical errors up to 100% were observed for ion energies above 10 eV. Finally, variabilities in the data resulted from the inhomogeneity of the naturally-occurring oxide surfaces and also from changes in secondary ion and electron emission during a measurement. As observed in Section 2.6.3, the yields of the electronegative species emitted from previously unirradiated samples varied up to a factor of three during a measurement while the metallic and metallic oxide species changed by less than ~25%. For the sputter-etched samples, the variability of the electronegative species was <25% and that of
the metallic species was <10% during a measurement.

These uncertainties would result in a serious loss of precision for quantitative measurements of energy spectra of mass-analyzed secondary ions. However, the objective of the measurements was to obtain qualitative complementary information to the mass spectrometric data presented in Chapter 2. The energy spectra are consistent with the results obtained with the mass spectrometer using the voltage modulation technique as a crude energy analyzer (Section 2.5.3.2) and also with the results observed by Becker et al. (Be83a). Thus, the spectra were not limited in usefulness by the noted uncertainties and they provide additional evidence that secondary ion emission during MeV projectile bombardment differs substantially from that observed during keV ion irradiations.
Figure 3.1 Cross sectional view of the electrostatic energy analyzer.
A  Outer Electrode
B  Inner Electrode
C  Retainer Segments
   •  Sapphire Beads
Figure 3.2 Experimental geometry for secondary ion energy distribution measurements. The analyzer was positioned at an angle of 45° with respect to the $^{79}$Br$^8+$ beam. An expanded view of the entrance structure of the analyzer is shown in the lower portion of the figure. Acceleration of the secondary ions to the analyzing energy (44.50 eV) occurs between Ni mesh grids in the entrance structure which are shown as a pair of dotted vertical lines in the figure.
75 MeV $^{79}\text{Br}^{8+}$

Electrostatic Energy Analyzer

CHANNELTRON

TARGET

ESA Entrance Structure (expanded view)
Figure 3.3 Schematic diagram of the electronics for the secondary ion energy distribution measurements with the analyzer operating in the constant transmission energy mode.
Figure 3.4 Results of a Monte Carlo simulation to determine the fractional resolution of the electrostatic energy analyzer. In this trial, ions of 50 eV were used and the pass energy of the analyzer was swept from 49.0 to 51.0 eV. The FWHM indicates a resolution of 1.28%.
Figure 3.5 Sample energy spectra obtained using (a) sector sweeping mode and (b) constant transmission energy mode during calibration of the energy analyzer with a Cs+ ion source. The FWHM of the peak in (b) is wider than that of (a) because in (b) the ions were accelerated to a pass energy of 44.50 eV while in (a) the pass energy was 17.50 eV.
Figure 3.6 Experimental determination of the pass energy-potential difference relationship of the energy analyzer. The data were obtained using the sector sweeping mode. The uncertainties in the data are smaller than the size of the data points. The slope of the line, which is the $E-\Delta V$ proportionality constant, was determined by a least-squares fit to the data to be $2.330\pm0.005$. The small negative $y$-intercept (-0.83 eV) is a result of contact potentials in the system.
Figure 3.7 Experimental determination of the fractional resolution of the energy analyzer. The data were obtained using the sector sweeping mode. The uncertainties in the data are smaller than the size of the data points. The slope of the line, which is the fractional resolution, was determined by a least-squares fit to the data (excluding the lowest energy point) to be $1.15\pm0.01\%$. The y-intercept of $0.14\pm0.01$ eV is a measure of the intrinsic width of the Cs$^+$ ion source.
Figure 3.8 Secondary ion energy spectra obtained from a Cu target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions prior to (dotted line) and after (solid line) sputter cleaning. For each of the energy spectra presented, the location of zero energy is approximately channel 76 but the exact location is uncertain due to the presence of contact potentials.
75 MeV $^{79}$Br$^{8+}$

- $\cdots$ Cu
- Cu (3 keV Ar Pre-sputtered)
Figure 3.9 Secondary ion energy spectra obtained from a Nb target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions prior to (dotted line) and after (solid line) sputter cleaning.
COUNTS/CHANNEL \( \times 10^3 \)

75 MeV \( ^{79}\text{Br}^{8+} \)

- Nb
- Nb (3 keV Ar Pre-sputtered)

CHANNEL

E=0 100 200 300 400 500

E=10 eV
Figure 3.10 Secondary ion energy spectra obtained from a Ta target bombarded by 75 MeV $^{79}$Br$^{8+}$ ions prior to (dotted line) and after (solid line) sputter cleaning.
75 MeV $^{79}$Br$^{8+}$

- Ta
- Ta (3 keV Ar Pre-sputtered)

Counts/Channel ($10^3$)

Channel

E = 0

E = 10 eV
The observation that the yields of Al\(^+\) and V\(^+\) secondary ions emitted during MeV projectile bombardment were proportional to the nuclear stopping power indicated the necessity of total sputtering yield measurements for neutral metallic atoms. This chapter describes a set of measurements of total yields for both keV and MeV projectiles and compares the results to the predictions of collision cascade theory (Si69, Wi75a, Section 1.3.1) and the semi-empirical formula of Matsunami et al. (Ma84, Section 1.3.2).

4.1 Collection of Sputtered Material

In these measurements, total sputtering yields and the angular distributions of sputtered particles were determined by collection, and subsequent analysis, of sputtered material on cylindrical catcher foils surrounding the target. The experimental geometry used during sputtering is shown schematically in Figure 4.1. For the high energy projectiles, 70 MeV \(^{79}\text{Br}\)\(^{7+}\) ions were used because of the extensive secondary ion data measured with that beam and energy (Sections 2.5.2 and 2.5.3). Primary beams of 100 keV \(^{40}\text{Ar}\)\(^+\) and 100 keV \(^{79}\text{Br}\)\(^+\) were also used so that more direct comparisons could be made with existing sputtering yield measurements. Initially, V was chosen as a target because our secondary ion data showed that the V\(^+\) ion intensities were consistent with a collisional production mechanism (Oc85b, Section 2.5.3). However, the low areal densities of sputtered V obtained with the 70 MeV Br beam could not be distinguished from intrinsic impurities on the catcher foils during Rutherford backscattering analysis (Section 4.2). Since Nb is chemically similar to V and since no intrinsic contaminants were present near mass 93, Nb was chosen as a target. In addition, with its larger Rutherford scattering cross section, it was detectable at significantly lower levels. Additional measurements were performed using a Y target.
bombarded by 70 MeV $^{79}$Br$^{7+}$ and 100 keV $^{40}$Ar$^{+}$ projectiles.

In all measurements, the projectiles were incident along the target normal. Sputtered material was collected on aluminum catcher foils mounted on the outside of a 304 stainless steel collector (Figure 4.2). Slots in the collector from $\theta=15^\circ$ to $\theta=90^\circ$, where $\theta$ is the measured from the target normal, determined the available area on the foil for the accumulation of sputtered material. The beams passed through 0.25" square holes cut in the catcher foil. The target and catcher foil assembly, designed to function as a Faraday cage, were electrically connected outside the vacuum chamber and biased to +600 V relative to the input of the beam current integrator (Figure 4.1). Secondary electron suppression was provided by a large negative bias applied to the grid (-2 kV for the 70 MeV Br beam and -500 V for the 100 keV beams). Although this configuration does not account for photoelectrons produced at the grid, the beam current was insensitive to the grid voltage over a wide range so we estimate errors of less than 2% in beam current integration.

For accurate sputtering yield measurements, the targets should be atomically clean. Therefore, prior to collections using the low-energy beams, an area of 0.08 cm$^2$ was sputter etched using the 100 keV $^{40}$Ar$^{+}$ beam. The beam was rastered in both the horizontal and vertical directions to insure uniform surface cleaning. This procedure was estimated to remove about 200 monolayers of material from the surfaces. During collections, beams with minimum current densities of 42.5 $\mu$A/cm$^2$ and 425 nA/cm$^2$ of Ar and Br, respectively, were incident on the central 0.02 cm$^2$ of the sputter-cleaned areas. At an operating pressure below 5 x 10$^{-9}$ Torr, these beam current densities ensured that the targets were dynamically clean throughout the collection runs.

For the 70 MeV $^{79}$Br$^{7+}$ irradiations, the 3 keV Ar ion gun was used to initially remove approximately 150 monolayers of material from an area of about 1 cm$^2$. The Br beam was then incident in the central 0.03 cm$^2$ of the sputter-etched area. However, the low beam fluxes produced by the tandem Van de Graaff accelerator (<1.8 x 10$^{12}$/cm$^2$/s) were not sufficient to guarantee that sputtering by the incident projectiles would keep the targets clean despite an
operating pressure below $5 \times 10^{-10}$ Torr. Therefore, at intervals of less than the monolayer adsorption time ($R_{\theta}82$) (neglecting the sputtering of the Br ions), the targets would be recleaned to remove at least an additional 50 monolayers of material. These cycles, two hours of collection and thirty minutes of cleaning, were repeated throughout the collection runs.

4.2 Analysis of Collected Material

The areal densities of Nb and Y on the catcher foils were measured as a function of $\theta$ (where $\theta$ is defined as in Figure 4.2) by Rutherford backscattering with either a 15 MeV $^{16}$O$^{3+}$ beam or an 850 keV $^4$He$^+$ beam. The choice of beam was determined by a number of competing practical considerations. The Al collector foils were quite pure in the bulk (purity >99.999%) but surface contaminants, apparently introduced during the manufacturing process, were detected near mass 56. For the 70 MeV $^{79}$Br irradiations, where both the fluence of incident ions and the sputtering yield were small, the density of collected material was near the level of these trace contaminants. Although the Rutherford scattering cross section for 850 keV $^4$He is approximately 20 times larger than that of 15 MeV $^{16}$O, the $^4$He beam has poor mass resolution for all but the lightest targets. As a result, the 15 MeV $^{16}$O beam was used for the analysis of these foils. (As noted previously, it was impossible to distinguish the V collected during 70 MeV Br bombardment from the trace impurities using either analysis beam.) For the 100 keV Ar and Br irradiations, the density of collected material was much larger and the 850 keV $^4$He beam should have been satisfactory. However, constraints in the analysis geometry with the use of this beam gave rise to relatively large uncertainties in the detector solid angle. As a result, only the foil with Nb sputtered by the 100 keV Br projectiles was analyzed by the 850 keV He beam.
4.2.1 Heavy Ion Rutherford Backscattering

The heavy ion backscattering analysis system is shown schematically in Figure 4.3. The catcher foils were mounted on a cylindrical target ladder of the same radius as the original collector. The ladder was attached to a vacuum feedthrough capable of both linear and rotary motion. A quartz viewer was mounted on the flat side of the target ladder to allow visual monitoring of the beam spot size, size, and position. Using two 1/16" collimators positioned at 128 cm and 49 cm from the target (not shown in Figure 4.3), a circular beam spot of <2 mm radius was obtained with beam currents ranging from 50 nA to 300 nA. To obtain accurate beam current integration, the target ladder was biased to +900 V, the electron suppression grid surrounding the target ladder was biased to -600 V, and each component was connected to the integrator through the bias battery. The Si surface barrier detectors (Ortec Model No. BA-19-150-300, Serial Nos. 15-247-F and 15-247-G) were located at an angle of 35.3° relative to the incident beam with each detector subtending a solid angle of 5.34±0.29 msr. The Rutherford scattering cross sections in the laboratory reference frame for Nb and Y were (7.15±0.21) x 10^{-25} cm^2/sr and (6.49±0.19) x 10^{-25} cm^2/sr, respectively.

The electronics used during data acquisition are shown schematically in Figure 4.4. The digital signals from the integrator were counted in a scaler. The signals from the detectors were processed to produce two types of pulses, data signals and event triggers. Data signals were pulses with voltage levels proportional to the charge generated by the detectors. The event triggers were pulses with a fixed voltage level independent of the detector-generated voltage levels.

Signals from the two detectors were processed in two channels. In each channel, pulses from the detector were pre-amplified, amplified, and split into two components. The first component (the data signal) was input into a delay amplifier to adjust the relative timing between the data signal and the event trigger. The linear gate stretcher shaped the pulse so that it was
compatible with the input requirements of the analog-to-digital converter (ADC1). The second component (the event trigger) was converted into a logic pulse, delayed, and input into both a scaler (event counter 1) and a special input of the Front End (Nu67). The event signal at the special input triggered an instruction to the IBM 4341 computer to read the ADC and scalers associated with that event (event counter 1 and the dead-time scaler for ADC1) and store the data in a computer-generated multichannel analyzer. Pulses from the second detector were handled similarly. All the data were also stored on magnetic tape for off-line analysis.

4.2.2 Alpha-Particle Rutherford Backscattering

The alpha-particle backscattering apparatus is shown schematically in Figure 4.5. The 850 keV $^4$He$^+$ beam was obtained from a 1 MV Van de Graaff accelerator located at the Sloane Physics Laboratory at Yale University. The collector foils were mounted on a cylindrical target ladder which was attached to a vacuum feedthrough capable of both linear and rotary motion. Using a 0.07" collimator, a circular beam spot of ~2 mm radius was obtained. To obtain accurate beam current integration, the target was biased to +600 V relative to the input of the beam current integrator (Elcor Model A309B). The annular surface barrier detector (Ortec Model TC-19-150-300, Serial No. 21-355-F) covered back angles from 170.3° to 175.5° and subtended a solid angle of 73.5±15.3 msr. This large uncertainty introduced an error into the total sputtering yield but not in the shape of the angular distribution since the solid angle was the same for all the data obtained with the 850 keV $^4$He beam. The Rutherford cross section in the laboratory reference frame was $(1.21±0.01) \times 10^{-23}$ cm$^2$/sr. Pulses from the detector were pre-amplified, amplified, and subsequently analyzed in a Northern Scientific TN-1705 multichannel analyzer.
4.2.3 Testing of the Backscattering Apparatus

As a check of the consistency of the analyses performed on the different accelerators, measurements were performed on both machines using a thin Au foil mounted on a C backing. The carbon foil was obtained from the Arizona Carbon Foil Company with a nominal thickness of 11.2±1.2 μg/cm². The Au was evaporated onto the C backing in a vacuum of about 10⁻⁵ Torr. The thickness of the Au foil was determined by measuring the energy loss of alpha particles through the foil. The measurements were performed using a ²¹⁰Po source mounted in an Alpha Particle Gauge (Ba65) and yielded a thickness of 50.5±5.1 μg/cm². This foil was then analyzed by both 15 MeV ¹⁶O³⁺ and 850 keV ⁴He⁺ Rutherford backscattering which gave thicknesses of 48.4±2.3 μg/cm² and 54±11 μg/cm², respectively. The consistency of the three measurements indicates that both of the analysis systems were accurate. (The large error in the alpha backscattering analysis was a result of the uncertainty in the solid angle subtended by the detector.)

4.3 Data Analysis

In order to translate the number of detected particles acquired during backscattering into areal densities of Nb and Y, the following expression, which is valid for thin films, was used (Ch78):

\[ A = Q(d\sigma/d\Omega)(d\Omega)(Nt) \]  \hspace{1cm} (4.1)

where \( A \) = total number of detected particles

\( Q \) = total number of incident particles

\( d\sigma/d\Omega \) = Rutherford scattering cross section in units of cm²/sr
\[ d\Omega = \text{solid angle of the detector} \]

\[ (N_t) = \text{number of target atoms per cm}^2. \]

Once the areal densities were determined, it was necessary to convert these quantities into angular distributions and total sputtering yields. Since the catcher foils used in these measurements were mounted in a cylindrical geometry around the target, the thin cylinder where sputtered material was collected may be taken to be a segment of the hemisphere of radius R generated by rotating the cylinder about the target normal. Since only a thin segment of the hemisphere is considered, the angle \( \theta \) defined as in Figure 4.2 is the direction of a sputtered particle as it leaves the surface of the target. Also, since the assumption of an isotropic collision cascade in an amorphous target implies that the angular distribution of sputtered particles is proportional to \( \cos \theta \) (Section 1.3.1), the measured areal densities were fit by a function of the form:

\[ f(\theta) = A \cos^B(\theta - \theta_c). \]  \hfill (4.2)

The parameter \( \theta_c \) was a measure of small misalignments in position during collection and analysis and was less than 6° in all of the measurements. To obtain the standard deviations of the parameters A and B, a weighted least-squares analysis (Be69) to the expression:

\[ \ln f(\theta') = \ln A + B \ln \cos(\theta') \]  \hfill (4.3)
To obtain the total number, \( N \), of sputtered atoms, \( f(\theta) \) is integrated over the hemisphere:

\[
N = 2\pi R^2 \int_0^{\pi/2} (A \cos^B(\theta')) \sin(\theta') \, d\theta' \quad (4.4)
= 2\pi R^2 A/(B+1)
\]

where \( R \), the distance between the target and the collector foil, is 1.59 cm. From the charge integration during collection, the number of incident ions is known so that the total sputtering yield can be obtained by dividing this number into the total yield of sputtered atoms.

4.4 Results

In Figures 4.6a and b, the angular distributions of Nb sputtered by 70 MeV \( ^{79}\text{Br}^7+ \) and 100 keV \( ^{79}\text{Br}^+ \) projectiles are shown. Table 4.1 presents the total sputtering yields and the fitting parameters, \( B \), obtained from each of the collector foils. Also included are the total sputtering yields predicted by the linear collision cascade theory (Si69, Wi75a, Section 1.3.1) and the semi-empirical formula of Matsunami et al. (Ma84, Section 1.3.2).

It is noted first that all of our results are consistent with the few published data obtained with similar beams of comparable mass. The over-cosine distributions (\( B>1 \)) are commonly observed for low energy projectile bombardment (Section 1.3.1, An85 and references therein) and have also been obtained in computer simulations of the sputtering process (Bi84, Sh85). The total sputtering yields for Nb obtained during 100 keV \( ^{40}\text{Ar}^+ \) and \( ^{79}\text{Br}^+ \) bombardment are consistent with yields measured from Nb targets under \( ^{40}\text{Ar} \) and \( ^{84}\text{Kr} \) bombardment at lower energies (An81 and Ma84 and references therein). At present, sputtering yield data for Y in this energy regime are not
available for comparison with our results.

For high-energy projectiles, sputtering yields are scarce for any metallic target or beam. However, yields ranging from 0.2 to 1.5 were measured for 67 MeV and 80 MeV I on Au (Ni76). These results are consistent with our values of 0.14±0.03 for 70 MeV Br on Nb and 0.14±0.04 for 70 MeV Br on Y since our lighter targets and projectile should give lower yields at a comparable beam energy. (We also note that the sublimation energy (which is often used as the surface binding energy) of Au (3.81 eV) is lower than that of either Nb (7.57 eV) or Y (4.37 eV).)

The sputtering yields measured during these experiments may also be compared to the predictions of the linear collision cascade theory (Si69, Wi75a, Section 1.3.1) and the semi-empirical formula of Matsunami et al. (Ma84, Section 1.3.2). These predictions agree to within approximately a factor of two with the measured yields for the 100 keV ion bombardments. Moreover, discrepancies of this magnitude between theoretical and experimental sputtering yields are common (An81, Ma84) and are a result of uncertainties in both the experimental measurements and the theoretical calculations. (We believe that the yield of 1.19±0.16 obtained during one of the 100 keV Ar irradiations of Y is low because a fraction of the sputtering beam struck the Al foil during collection (Section 4.5.3).)

Comparison of the measured Nb and Y yields for 70 MeV Br bombardment with the model predictions is not as straightforward as for the 100 keV ion irradiations. As noted in Section 1.3.2, comparison of the predictions of Matsunami et al. (Ma84) with our high energy results is inappropriate because our bombardment conditions were substantially different from those considered in the derivation of eq. (1.2). The predictions of the collision cascade theory, however, are suitable for comparison with our results. For ions in the Rutherford scattering regime, \( \alpha \) in eq. (1.1) is equal to 1/2 (Si69) assuming only elastic collisions. With this assignment for \( \alpha \), cascade theory predicts yields of 0.47 for Nb and 0.77 for Y during 70 MeV Br bombardment. These
predictions are considerably higher than the measured yields of 0.14±0.03 and 0.14±0.04 for Nb and Y, respectively. However, when inelastic collisions are considered, the value of α and, therefore, the predicted sputtering yield decreases (Si71), giving better agreement with the measured values. These results are discussed further in Section 5.1.

4.5 Error Analysis

Although the collection of sputtered material and subsequent analysis by Rutherford backscattering were straightforward, there were several possible sources of error during the measurements. With the exception of changes in surface topography during ion bombardment and effects of surface crystallinity, these uncertainties were quantifiable. The errors in beam current integration, the solid angles of the detectors, and the Rutherford cross sections were presented above. Statistical errors for the areal densities obtained during backscattering analysis were less than 7% for each case. The remaining uncertainties are discussed below.

4.5.1 Alignment of the Apparatus

During the collection of sputtered material, small misalignments (<1 mm) in the positions of the targets and catcher foils were unavoidable. Griffith (Gr79) has examined this problem in detail and has shown that small deviations in position during collection cause some changes in the shape of the angular distribution but that the integration of the differential yield was insensitive to this error (<2%). However, the uncertainty in R (eq. (4.4)) due to misalignments introduces an error in the total yield which has been included in the results presented in Table 4.1.

A larger misalignment of the Al catcher foils used during one of the 100 keV Ar irradiations of the Y target was also observed. As discussed in Section 4.1, if some of the projectiles struck the
catcher foil during a collection run, they would be detected as beam on target resulting in a lower measured yield. Despite the precautions used to avoid this problem, the beam spot on the Y target showed that the beam had been partially blocked during collection. Since the other beam spots showed no indication of the beam striking the collector foils, this is a reasonable explanation for the discrepancy in the two values for the sputtering yield for 100 keV Ar bombardment of Y.

During analysis measurements, small misalignments during mounting of the collector foils on the target ladder were minimized by having the collector assembly and the backscattering target ladder similarly shaped. As a result, the values of $\theta_c$ (eq. (4.2)) resulting from this uncertainty were less than $6^\circ$ during each of the measurements.

4.5.2 Sputtering by the Analysis Beams

The 15 MeV $^{16}\text{O}^{3+}$ and 850 keV $^4\text{He}^+$ projectiles sputtered a fraction of the collected material from the $\text{Al}_2\text{O}_3$ surface of the catcher foil during the backscattering analysis measurements. If this fraction were a substantial portion of the collected material, a serious systematic error would result. Using eq. (1.1), the sputtering yield for the beams on $\text{Al}_2\text{O}_3$ are estimated to be approximately $5.4 \times 10^{-3}$ for 15 MeV $^{16}\text{O}$ and $1.3 \times 10^{-3}$ for 850 keV $^4\text{He}$. For the material collected during the 100 keV ion irradiations, the total amount of material removed was less than 5% during heavy-ion backscattering and less than 0.1% during alpha backscattering. For the foils used during the 70 MeV Br bombardments, the $^{16}\text{O}$ beam removed less than 10% of the material during each analysis run. This amount was within the uncertainties noted above. In addition, repeat measurements at $\theta=30^\circ$ and $\theta=50^\circ$ for the foil with Nb sputtered by 70 MeV $^{79}\text{Br}^{7+}$ yielded results which agreed within error (Figure 4.6a).
4.5.3 Deviation of the Scattering Cross Section from Rutherford

In order to insure that the use of the Rutherford cross section during 15 MeV $^{16}\text{O}^{3+}$ and 850 keV $^{4}\text{He}^+$ backscattering did not introduce significant errors into the measurements, the amount of electronic screening of the target and projectiles based on the Thomas-Fermi model was calculated for each beam. Torrens (To72) has calculated the degree of screening as a function of the ratio of the distance of closest approach during a collision, $d_0$, to the screening radius, $a$, where $a=0.885a_0(Z^{2/3} + Z'^{2/3})^{-1/2}$ and $a_0$ is the Bohr radius. For 15 MeV $^{16}\text{O}$ scattered from Nb at 144.7°, $d_0=32$ fm and $a=0.12$ Å which implies less than a 1% degree of electronic screening. A similar result is obtained for scattering from Y on the catcher foils. For 850 keV $^{4}\text{He}$ scattered from Nb at 172.9°, $d_0=139$ fm and $a=0.13$ Å which implies a screening of less than 2%. These errors are negligible in comparison with the other uncertainties in the measurements.

4.5.4 Sticking Probabilities of Sputtered Atoms on Metallic Surfaces

When a sputtered particle strikes one of the catcher foils or the exposed sections of the stainless steel collector, it might bounce off rather than be trapped. Therefore, for an accurate measurement, the sticking probability must be known. Weller and Tombrello (We80) have measured a sticking fraction of 0.97±0.03-0.08 for Nb sputtered by 80 keV Ar onto $\text{Al}_2\text{O}_3$. Since the surfaces of our catcher foils were also $\text{Al}_2\text{O}_3$, we assumed a unity sticking probability of sputtered Nb onto our foils which should be accurate to within approximately 5%. A unity sticking fraction for Y onto $\text{Al}_2\text{O}_3$ was also used although this assignment was not as certain (no measured values were available for comparison).

Another number of interest is the sticking fraction of either Nb or Y onto stainless steel. If
this fraction is small, a significant number of the sputtered particles may reflect off the collector and the target ladder and strike the section of the catcher foil that was not nominally in use (Figures 4.1 and 4.2). Analysis of the foil used during 100 keV $^{79}$Br$^+$ bombardment of Nb, where only one section of the foil was nominally used, indicated that this effect was significant at forward angles during the measurement (about 20% of the principal collector foil areal density). This indicates a sticking fraction perhaps as low as 50% for sputtered Nb onto stainless steel. This effect could have been a problem during the 70 MeV Br irradiations because only one collector foil was used (sputtered Nb was collected on one section and Y was collected on the other (See Figure 4.2)). However, the mass resolution of the 15 MeV $^{16}$O beam was sufficient to distinguish any cross-talk between the sputtered Nb and Y so this effect was not a problem in determining the sputtering yields.
Table 4.1 Measured sputtering yields from Nb and Y targets under various bombardment conditions. The parameter B, which is a measure of the steepness of the angular distribution, and the predictions of sputtering yields of the linear collision cascade theory (Si69, Wi75a) and of a semi-empirical formula (Ma84) are also shown. The errors quoted represent quantifiable experimental uncertainties (one standard deviation) but do not include systematic variabilities associated with the crystallinity or topography of the target surface.
### Table 4.1

<table>
<thead>
<tr>
<th>Target</th>
<th>Beam</th>
<th>Energy</th>
<th>B</th>
<th>Measured Yield</th>
<th>Cascade</th>
<th>Matsunami et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>$^{79}$Br</td>
<td>70 MeV</td>
<td>1.53±0.10</td>
<td>0.14±0.03</td>
<td>0.47</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>$^{40}$Ar</td>
<td>100 keV</td>
<td>1.06±0.05</td>
<td>1.73±0.23</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Nb</td>
<td>$^{40}$Ar</td>
<td>100 keV</td>
<td>1.34±0.07</td>
<td>1.42±0.19</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>Nb</td>
<td>$^{79}$Br</td>
<td>100 keV</td>
<td>1.15±0.18</td>
<td>2.71±0.47</td>
<td>4.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Y</td>
<td>$^{79}$Br</td>
<td>70 MeV</td>
<td>1.08±0.16</td>
<td>0.14±0.04</td>
<td>0.77</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>$^{40}$Ar</td>
<td>100 keV</td>
<td>0.97±0.06</td>
<td>2.00±0.27</td>
<td>3.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Y</td>
<td>$^{40}$Ar</td>
<td>100 keV</td>
<td>1.20±0.07</td>
<td>1.19±0.16</td>
<td>3.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 4.1 Experimental geometry used during sputtering. The primary beam was incident along the target normal. Sputtered material was collected on a cylindrical Al foil. The target and catcher foil formed a Faraday cage which was biased at +600 V. Secondary electron suppression was provided by a large negative bias applied to the grid (-2 kV for the 70 MeV Br beam, -500 V for the 100 keV beams).
Figure 4.2 Schematic diagram of the catcher foil assembly. The distance from the target to the collector foils, $R$, is 1.59 cm. Sputtered material was collected on an Al catcher foil which was mounted on the outside of the stainless steel collector and which subtended an angle from $\theta=15^\circ$ to $\theta=90^\circ$, where $\theta$ is measured from the target normal.
Figure 4.3 Schematic diagram of the heavy ion Rutherford backscattering analysis system.
15 MeV $^{16}\text{O}^{3+}$

SURFACE BARRIER DETECTOR

ELECTRON SUPPRESSION GRID

TARGET HOLDER

TARGET

SURFACE BARRIER DETECTOR

- 600 V

+ 900 V

CURRENT INTEGRATOR
Figure 4.4 Schematic diagram of the electronics used during 15 MeV $^{16}\text{O}^{3+}$ Rutherford backscattering analysis. Signals from the detector were amplified and shaped to produce logic and linear pulses. The logic pulses were both counted in a scaler (Event Counter) and used as "event" pulses to tell the computer when to read the contents of the analog-to-digital converter (ADC1). (TSCA - Timing Single Channel Analyzer, LGS - Linear Gate Stretcher, GDG - Gate and Delay Generator).
Figure 4.5 Schematic diagram of the alpha-particle backscattering analysis system.
Figure 4.6 Angular distributions of Nb sputtered by (a) 70 MeV $^{79}$Br$^7+$ and (b) 100 keV $^{79}$Br$^+$. The solid curve is a fit to a function of the form: $A \cos^B(\theta - \theta_c)$ where in (a) $B=1.53 \pm 0.10$ and $\theta_c = 3^\circ$, and in (b) $B=1.15 \pm 0.18$ and $\theta_c = 0.8^\circ$. 
AREAL DENSITY ($10^{13}$/cm$^2$)

$\theta$ (DEGREES)
CHAPTER 5
DISCUSSION OF RESULTS AND CONCLUSIONS

In this chapter, the results of our measurements will be discussed in light of the models that have been proposed to describe sputtering and secondary ion emission during keV projectile bombardment of metallic surfaces (Sections 1.3 and 1.4). Other possible models to describe the results obtained for secondary ion emission of non-metallic species during MeV heavy ion bombardment will also be presented. The chapter closes with some proposals for future experiments which supplement the results presented here. In particular, a number of measurements which may further elucidate the mechanism for the production of non-metallic secondary ions during MeV ion irradiations are discussed.

5.1 Comparison of Total Yields and Secondary Ion Emission Data with Collision Cascade Theory

In Section 1.3, the linear collision cascade theory of sputtering was presented. As discussed, sputtering in this model is described in terms of elastic collisions between the projectiles and the target atoms. Consequently, the total yield of sputtered particles is determined by the nuclear stopping cross section for the projectile in the target (eq. (1.1)). The energy distribution of sputtered atoms is predicted to peak at low energies and to decrease slowly as the energy of the sputtered atom increases. In addition, the assumption of an isotropic collision cascade in an amorphous target implies that, for perpendicularly incident projectiles, the sputtered particles are emitted in a cosine distribution around the target normal.

In order to test the predictions of this theory for high energy ion irradiations, the total yields and angular distributions of Nb and Y atoms were measured for atoms sputtered during 70 MeV $^{79}\text{Br}^{7+}$ and 100 keV $^{40}\text{Ar}^{+}$ and $^{79}\text{Br}^{+}$ bombardments. (It was not possible to measure neutral atom
energy spectra with our apparatus. While the angular distributions were, in general, more sharply peaked than a simple cosine distribution, the sputtering yields were consistent with the predictions of eq. (1.1) (see Table 4.1 and Section 4.4). This agreement indicates that collisional sputtering is the dominant mechanism for the sputtering of metals during high energy projectile bombardments. This result is supported by measurements of self-sputtering of Au targets with projectile energies up to 20 MeV (Ba76b) and sputtering of Au by 67 MeV and 80 MeV I (Ni76). In these experiments, the measured yields were consistent with a collisional description of the sputtering process when non-linear effects were included.

The predictions of collision cascade theory were also compared with our results for the emission of atomic metallic secondary ions. For 10-90 MeV $^{79}$Br bombardment of a V target, the slope of the nuclear stopping cross section of Br in V agreed remarkably well with the measured intensities of the V$^+$ secondary ions (Figure 2.16a). For 50-250 keV and 2.8-40 MeV $^{79}$Br irradiations of Al and V, the intensities of Al$^+$ and V$^+$ secondary ions were also observed to be roughly proportional to $S_N(E)$ across the entire projectile energy range (Figures 2.20a and 2.21a). These results indicate that the production of these ions was also a consequence of a collision cascade. This conclusion is supported by the observation that the yields of Al$^+$ and Cu$^+$ secondary ions from targets bombarded by $^{252}$Cf fission fragments also were proportional to $S_N(E)$ (Kn82). In addition, the energy distributions of metallic secondary ions emitted during MeV ion irradiations were consistent with those observed for collisionally-generated secondary ions, i.e. the distributions peak at a few eV and decrease slowly for increasing ion energy (Be83a).

A significantly different conclusion is obtained from a comparison of the predictions of collision cascade theory with our results for the emission of positive secondary ions of electronegative surface constituents. Substantial numbers of these secondary ions, especially $^{16}$O$^+$, were observed from each oxidized target during MeV ion bombardments (Figures 2.9-2.15). More importantly, however, the ion yields increased substantially as the energy of the projectile
increased from 100 keV to 20 MeV while above this energy, the yields were approximately independent of projectile energy (Parts b and c of Figures 2.16, 2.20-2.22). This trend is to be contrasted with the behavior of \( S_N(E) \) across this energy range (See Figure 2.20a). In addition, essentially all of these secondary ions had energies below 20 eV while energy distributions of collisionally-generated ions extend out to \(-1 \) keV. These observations clearly demonstrate that the positive secondary ions of electronegative species observed during MeV ion irradiations were not produced as a result of collision cascades.

5.2 Comparison of Secondary Ion Data with Models of Secondary Ion Emission for Low Energy Ion Bombardment

In Section 1.4, the most reproducible observations of secondary ion emission that have been reported during keV ion bombardment of metallic surfaces were presented. A number of models, which can be classified as thermal, chemical, or quantum mechanical, that have been proposed to describe these observations were also discussed. The validity of the general observations and the applicability of the proposed models to our results for secondary ion emission during MeV projectile bombardment are discussed below.

5.2.1 Thermodynamic Models

The thermodynamic models of secondary ion formation developed by Andersen and Hinthorne (An73, An75a), by Jurela (Ju73), and by Williams (Wi79a) are able to explain the observation that, for keV projectiles, positive ion yields of elements sputtered from a common matrix exhibit an inverse exponential dependence on the ionization potential of the sputtered atom (Observation #1, Section 1.4). However, the results presented in Chapter 2 demonstrate that this
observation is not valid for metallic surfaces bombarded by MeV heavy ions. As noted above, a
significant enhancement was observed in the production of positive secondary ions from
electronegative target constituents. In particular, the intensities of \( O^+ \) secondary ions emitted from
the naturally-occurring oxide surfaces were comparable to the intensities of the metallic secondary
ions for all of the targets used in the experiments.

Since the thermal models of secondary ion formation only predict the ion/neutral ratio of
sputtered particles and since the neutral yields of the electronegative species may also be
enhanced during MeV projectile bombardment, the results noted above do not conclusively
eliminate these models as possible descriptions of secondary ion emission at high bombarding
energies. However, the lack of validity of Observation #1 for MeV projectiles implies that the ion
emission mechanisms included in these models are unlikely to accurately represent the physical
situation that is present during the high energy irradiations.

5.2.2 Chemical Models

For keV projectile bombardment, the presence of oxygen or other electronegative species
at the surface of a metal significantly enhances the production of positive metallic secondary ions.
Similarly, the presence of cesium or other electropositive species at the surface enhances the yield
of negative metallic secondary ions (Observation #2, Section 1.4). Included among the models
proposed to explain these observations are the bond breaking model of Slodzian (Si75), the
molecular model of Thomas (Th77), and the surface polarization model of Williams and Evans
(Wi76). Although the secondary ion emission mechanisms differ in the three models, in each case
oxygen ions which are sputtered from the surface are predicted to be predominantly negatively
charged. For keV projectiles, this prediction is supported by substantial evidence (see, for
example, (Mü73), (Mü74), (Be75)). The trace yields of \( O^+ \) secondary ions that were observed in our
measurements using 50-250 keV projectiles (Figures 2.12-2.16, and 2.20-2.23) are also consistent.
with this prediction. However, significant numbers of O$^+$ secondary ions were observed during MeV heavy ion bombardment of similarly-prepared surfaces (Figures 2.12-2.15). This result, coupled with the observation of intense signals of positive secondary ions from other electronegative species, e.g. F$^+$ and Cl$^+$, indicates that the chemical models are not capable of describing secondary ion emission from metallic surfaces during MeV ion bombardment.

5.2.3 Quantum Mechanical Models

As noted in Section 1.4.3, the production of multiply-charged secondary ions of Al and Si during keV ion bombardment is well described in terms of the kinetic emission model of Joyes (Jo69, Jo73). In this model, some of the collisions which occur during the cascade are violent enough to produce an inner shell vacancy in one of the colliding atoms. The mechanism for the removal of the core electron is described by the molecular orbital promotion model of Fano and Lichten (Fa65, Li67). If the atom with the vacancy is sputtered before the vacancy is filled, the atom will Auger decay in the vacuum. Although most of these decays will produce singly-charged metallic ions, multiply-charged ions may also be generated when the electronic excitation energy is sufficiently large.

In our measurements, multiply-charged secondary ions were only observed during MeV ion bombardment of the oxidized Al target. As shown in Table 2.1 and Figure 2.12, a significant number of Al$^{2+}$ secondary ions were observed during 70 MeV $^{79}$Br irradiation of a sputter-etched sample. Small, but statistically significant, intensities of Al$^{3+}$ and O$^{2+}$ ions were also seen. If these ions were generated by the kinetic mechanism of Joyes (Jo69, Jo73), the energy distribution of the ions should be typical of those created during a collision cascade. The Al$^+$, Al$^{2+}$, and Al$^{3+}$ ion energy distributions that have been observed by Becker et al. are consistent with a collisional energy spectrum (Be83a). However, as noted in Section 2.5.3.2, essentially all of the O$^+$ secondary ions have energies below 20 eV. Thus, it is unlikely that the O$^+$ or O$^{2+}$ secondary ions
observed in our measurements were produced in a manner consistent with the kinetic mechanism.

In addition, the molecular orbital promotion model predicts that in a collision between atoms of different elements, the inner shell vacancy is more likely to be produced on the lighter colliding partner (Ba72). The absence of O* or O2* signals with energy distributions that are characteristic of a collision cascade would seem to indicate that the Al2* and Al3* ions were not produced as a result of asymmetric collisions between recoiling Al and O atoms during the cascade. However, if the lifetime of an inner shell vacancy in oxygen is substantially shorter than the ejection time of a sputtered atom (~10^{-14} - 10^{-13} s), few oxygen secondary ions produced by the kinetic mechanism would have been observed in our measurements. In fact, this situation appears to have occurred (assuming that the multiply-charged Al ions were generated by the kinetic mechanism). For previously unirradiated Al samples, i.e. Al2O3 surfaces, no statistically significant Al2* signal was observed during 50 and 100 keV 79Br bombardment while for 2.8-40 MeV projectiles, substantial numbers of Al2* ions were seen. The keV data are consistent with previous measurements using low energy projectiles where the presence of oxygen on Al surfaces was observed to decrease the yield of Al2* ions (Jo73 and references therein) and with the prediction that asymmetric Al-O collisions are less effective in producing Al2* inner shell vacancies. Since the surfaces used in the MeV ion irradiations were similarly prepared, it would be expected that a similar yield of Al2* ions would be observed. However, intense Al2* signals were seen with the MeV projectiles. Therefore, if the Al2* and Al3* secondary ions observed in our measurements were produced by the kinetic mechanism, a significant fraction of the Al inner shell vacancies were produced as a result of asymmetric collisions.

Perhaps a more significant observation is the fact that the Al2* yield was approximately constant for 2.8-40 MeV 79Br bombardment while the Al* yield was substantially decreasing (Figures 2.20a and d). (Similar trends in Al* and Al2* emission have been seen during bombardment of sputter cleaned Al foils by 252Cf fission fragments (Kn82).) This result indicates that production of the multiply-charged secondary ions is due to direct impacts with either the
projectile or fast recoil atoms. In addition, the number of these violent collisions varies only slightly as the energy of the projectile increases and is not directly related to the nuclear stopping cross section. Since these hard collisions would be expected to occur early in the cascade, the multiply-charged species must also be formed in the early stages of the collision cascade. In contrast, the observation that the Al\textsuperscript{+} ion intensities are roughly proportional to \( S_N(E) \) indicates that the singly-charged species are formed at later stages of the cascade.

The second quantum mechanical model discussed in Section 1.4 was proposed by Williams to explain his observations of enhanced emission of F\textsuperscript{+} and Cl\textsuperscript{+} secondary ions during 2-10 keV Ar\textsuperscript{+} and O\textsubscript{2}\textsuperscript{+} bombardment of fluorinated Si and chlorinated Al, respectively (Wi81). In this model, which Williams termed ion-stimulated desorption, the F\textsuperscript{+} secondary ions were postulated to be produced as a result of electron-stimulated desorption events of the Knotek-Feibelman type (Kn78). These events were initiated by a collisionally-generated Si LW Auger electron from a silicon atom which was not the nearest neighbor of the ejected fluorine atom. (The situation is analogous for Cl\textsuperscript{+} emitted from Al.)

Williams' ion emission mechanism may be compared with our observations of enhanced emission of positive secondary ions from electronegative surface constituents during MeV ion bombardment. Similar to Williams' results, the emitted electronegative species were observed to have very low energies. As noted in Section 2.5.3.2, essentially all of the O\textsuperscript{+} secondary ions have energies below 20 eV. Also, the integrated ion energy distributions presented in Figures 3.8-3.10 demonstrate the dominance of low energy secondary ions. In contrast to Williams' results, however, for 2.8-40 MeV \(^{79}\text{Br}\) irradiation of the Al target, the yield of O\textsuperscript{+} ions did not scale as a function of projectile energy in the same manner as the yield of the Al\textsuperscript{2+} ions. In Williams' measurements, the observation that the F\textsuperscript{+} yield scaled with both the yield of Si\textsuperscript{2+} and the yield of Si (LWW) Auger electrons was a crucial factor in support of the ion-stimulated desorption mechanism. The lack of such a correlation in our data indicates that the positive ions from electronegative species that we
have observed are not produced as a result of electron-stimulated desorption events induced by Auger electrons from non-nearest metallic atoms.

5.3 Other Possibilities

Since the emission of positive secondary ions of electronegative species is significantly enhanced during MeV ion irradiations, it is important to determine if the mechanism which produces these ions is proportional to $S_E(E)$. As noted in Section 2.5.3.4, for 10-90 MeV Br in V, $S_E(E)$ increases by about a factor of three (No70, Zi80). However, the O+ ion yield remained approximately constant (Figure 2.16b). Also, for 2.8-40 MeV Br bombardment of Al, V, and Y, the increase in the yields of the electronegative species as the projectile energy increased from 2.8 to 20 MeV was greater than the rise in $S_E(E)$. Above 20 MeV, the yields were approximately independent of projectile energy (Parts b and c of Figures 2.20-2.22). These observations clearly demonstrate that the yield of these ions is not directly related to the total energy deposited in electronic excitation.

In Section 2.5.3.4, it was observed that both the primary ionization for Br in V and the intensity of O+ emission from a V target varied slowly for Br energies above 10 MeV (see Figure 2.16b). It was also noted that this similarity was consistent with the hypothesis that a significant fraction of the O+ ions were being desorbed as a result of electronic transitions induced by fast secondary electrons. (This hypothesis is similar, in principle, to the model of ion-stimulated desorption proposed by Williams.) In order to test this hypothesis, the primary ionization, calculated as in (Fi75), has been superimposed on the O+ data of Figure 2.21b. It is clear that, apart from the approximately constant behavior above 20 MeV, there is poor agreement between the experimental data and the primary ionization. Poor agreement was also obtained for the emission of each of the electronegative species from each target. Thus, it is unlikely that the production of
non-metallic secondary ions is proportional to the number of secondary electrons directly created by the primary beam. (Becker et al. (Be83a) have observed a similar lack of agreement in a comparison of the estimated ionization cross sections, which were obtained from an extrapolation of direct Coulomb ionization of heavy targets by high energy protons (using the semi-classical approximation model (Ha75)), with H$_1^+$ yields measured during $^{58}$Ni bombardment of Al and Sc targets for projectile velocities from 0.2-1.4 cm/ns.)

Another interesting possibility for the desorption of these ions has been suggested by Krueger (Kr79). After entering the target, the fast projectiles rapidly lose electrons and become highly charged. The strong resultant Coulomb field will ionize individual core electrons and also collectively excite valence electrons near or in the conduction band. This collective excitation may be considered as a polarization of the electron plasma which is able to desorb ions via a sudden perturbation at the surface. Although Krueger does not predict the energy dependence of the desorption yields, it may be expected that the cross sections will scale with the square of the effective charge, $Z_{\text{eff}}^2$ may be calculated using the empirical formula of Heckman et al. (He60). As seen in Figure 2.21b for the V target, reasonable agreement between the O$^+$ data and $Z_{\text{eff}}^2$ is obtained for Br energies below 10 MeV. In fact, in a least-squares fit of $A^*Z_{\text{eff}}^n$ (where A and n are adjustable parameters) to the O$^+$ data for each target below 10 MeV, n was found to be consistent with 2 in each case. Becker et al. have also observed similar agreement at low projectile velocities (<0.8 cm/ns) in a comparison of $Z_{\text{eff}}^2$ with H$_1^+$ ion yields obtained from Al and Sc targets bombarded by $^{58}$Ni (Be83a). Unfortunately, in our data, the agreement of $Z_{\text{eff}}^2$ with the trend in F$^+$ and Cl$^+$ emission is poor at all energies. Therefore, these results indicate that this mode of desorption is not the universal mechanism for the production of the non-metallic secondary ions.

Another model that relates the number of secondary electrons generated by the incident projectiles to the desorption of large biomolecules has recently been proposed by Hedin et al.
(He85). In this model, which was derived from the "hit" theory of radiation biology, desorption requires that a molecule be hit by a number of secondary electrons. The authors do not specify the precise desorption mechanism but only assume that desorption is caused by the secondary electrons. (Hedin et al. do state that the model suggests that the desorption is due to the breaking of bonds by the shower of secondary electrons generated by the passing ion.) With this model, Hedin et al. are able to describe the dependence of the desorption yields of a number of biomolecular ions on molecular mass and also on projectile velocity over a wide range. This model, although interesting, is limited in its applicability to our data because several assumptions that are implicit in the model are only suitable for biomolecular solids.

An additional hypothesis that may be considered is that the secondary ions observed in our measurements were desorbed neutral atoms that were ionized in the vacuum by fast secondary electrons. This hypothesis would imply that the yield of secondary ions should be proportional to the total yield of neutral particles. This result is consistent with the observations for Al+ and V+ secondary ions since the yield of these ions was approximately proportional to \( S_N(E) \) (Figures 2.16a, 2.20a, 2.21a) but not with the yield of Y+ ions since the number of these ions was approximately constant for 2.8-40 MeV Br projectiles (Figure 2.22a). For the non-metallic ions, it is not possible to determine whether this hypothesis is correct without measurements of the neutral yields of these species. However, since the yield of the non-metallic ions increases substantially as the Br energy increases from 100 keV to 10 MeV, a similar increase must be observed in the neutral yield. As a result, an additional mechanism would be necessary to account for the increase in the desorption of neutral non-metallic particles from the surface.

We note, finally, that none of the models that we have discussed are capable of fully explaining both the enhancement in the emission of positive secondary ions of electronegative species during MeV projectile bombardment and the variation of the yields of these species as a function of the projectile energy. The data presently available, however, are not sufficient to
identify unambiguously another ion formation mechanism.

5.4 Future Experiments

The observations noted in Section 5.1 have shown that the sputtering of metals during MeV heavy ion bombardment is consistent with a collisional description of the sputtering process. Similarly, the data for metallic secondary ion emission indicates that these ions are produced as a result of a collision cascade. In order to test these conclusions, several possible experiments may be performed. First, measurements of the energy spectra of neutral metallic atoms sputtered during MeV ion bombardment would test the $E^{-2}$ behavior that is predicted by cascade theory with the asymptotic dependence of these distributions. Second, systematic measurements of total sputtering yields of metals across a wide range of MeV projectile energies would conclusively determine whether the yields are proportional to $S_N(E)$ as predicted by eq. (1.1). For a similar reason, total yields of metallic secondary ions emitted from atomically-clean surfaces should be measured as a function of projectile energy. In addition, with these measurements, the inference that the ionization probabilities of sputtered Al and V is constant across a wide range of beam energies (Sections 2.5.3.4 and 2.6.3) may be tested for a number of metallic surfaces.

Additional studies of non-metallic secondary ion emission during MeV ion irradiations of targets that have been prepared and characterized in vacuo are especially necessary in order to obtain new insight into the formation mechanisms of these ions. In order to further test the possibility that the non-metallic ions are produced by secondary electrons, simultaneous investigations of both secondary ions and electrons (with particular emphasis on any variations of the secondary electron spectrum with projectile velocity) are crucial. Also, comparative measurements of electron and ion bombardment of both maximal-valency and non-maximal valency ionic solids (e.g., TiO$_2$ and Ti$_2$O$_3$) should determine whether electron-stimulated desorption events
of the Knotek-Feibelman (Kn78) type are important in the emission of these ions.

Additional information would be obtained in systematic studies of O+ emission as a function of projectile velocity, as a function of projectile charge state, and induced by a series of projectiles with the same velocity but with increasing atomic number. Comparative studies of O+ and F+ emission from oxygenated and fluorinated metallic surfaces as well as a comparison of O+ and O- ion emission from the same sample are also necessary. Also, measurements of mass-analyzed secondary ion energy distributions of both the positive and negatively charged electronegative species should be performed. In addition, as noted in Section 2.5.3.3, measurements of O+ emission as the work function of the surface is slowly varied are an interesting area of future research.

Finally, and perhaps most importantly, we note that this work has demonstrated that future theoretical investigations of secondary ion emission must address the important role of the projectile energy in determining the relative yields of various sputtered ions.
Bibliography

An72  C.A. Andersen, Science 175 (1972) 853.
Be75  A. Benninghoven, Surf. Sci. 53 (1975) 596.
Bi76 A. Blandin, A. Nourtier and D.W. Hone, J. Physique 37 (1976) 369.
Gr53 W.R. Grove, Philos. Mag. 5 (1853) 203.
Ha75 J.M. Hansteen, O.M. Johnsen, and L. Kocbach, Atomic Data and Nuclear Data Tables 15 (1975) 305.
He68a  J.-F. Hennequin, J. Physique 29 (1968) 1053.
Ku79  E.A. Kurz, Amer. Lab. — (1979) —.
Pu38  E.M. Purcell, Phys. Rev. 54 (1938) 818.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Author(s)</th>
<th>Title and Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa20</td>
<td>M.N. Saha</td>
<td>Phil. Mag. 40 (1920) 472.</td>
</tr>
<tr>
<td>Sa21</td>
<td>M.N. Saha</td>
<td>Z. Phys. 6 (1921) 40.</td>
</tr>
<tr>
<td>St72</td>
<td>G. Staudenmaier</td>
<td>Rad. Eff. 13 (1972) 87.</td>
</tr>
<tr>
<td>Th10</td>
<td>J.J. Thompson</td>
<td>Phil. Mag. 20 (1910) 752.</td>
</tr>
<tr>
<td>Th68</td>
<td>M.W. Thompson</td>
<td>Phil. Mag. 18 (1968) 377.</td>
</tr>
</tbody>
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