EMISSION OF POSITIVE OXYGEN IONS FROM BOMBARDMENT OF ADSORBATE-COVERED METAL SURFACES

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Abstract

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During ion bombardment of metal surfaces, collision cascades can result in the emission of sputtered secondary ions. Recent experiments, however, have suggested that the emission of positive ions of electronegative adsorbates can result from electronic processes rather than from processes involving elastic collisions. This dissertation presents the results of experiments studying the emission of positive oxygen ions from oxygen- and carbon-monoxide-covered transition metal surfaces during bombardment by 25-250 keV ions of neon, argon, and krypton.

The systems studied may be grouped into four categories. For a nickel substrate with adsorbed oxygen, the emission of positive oxygen ions proceeds through collision cascades. For titanium and niobium with adsorbed oxygen, the emission of positive oxygen ions is proportional to the primary ion velocity, consistent with emission from electronic processes; for a given primary ion velocity, the oxygen ion yield is independent of primary ion species. For substrates of molybdenum and tungsten, the oxygen yield is proportional to primary ion velocity, but the yield also depends on the primary ion species for a given primary ion velocity in a manner that is consistent with emission resulting from electronic processes. For these two groups, except for titanium, the yields during neon ion bombardment do not extrapolate (assuming linearity with primary ion velocity) to a nonzero
value at zero beam velocity. The magnitude of the oxygen ion yields from these targets is not consistent with that expected if the emission were induced by secondary electrons emitted during the ion bombardment. The emission of positive oxygen ions from carbon monoxide adsorbed onto nickel surfaces is not a simple function of primary ion velocity and species, although the emission certainly does not result from collision cascades. Finally, the emission from carbon monoxide adsorbed onto palladium surfaces resembles that for the oxidized surfaces (excepting nickel).
Emission of Positive Oxygen Ions from Ion Bombardment of Adsorbate-Covered Metal Surfaces

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TABLE OF CONTENTS

Acknowledgments ........................................................................................................ii
Table of Contents ..........................................................................................................iv

CHAPTER ONE: INTRODUCTION .............................................................................. 1
  1.1. General Introduction ......................................................................................... 1
  1.2. Emission of Secondary Ions ............................................................................ 3
    1.2.1. Sputtering Theory ..................................................................................... 4
    1.2.2. Ionization Theory ..................................................................................... 7
  1.3. Positive Ions of Electronegative Elements ...................................................... 11
  1.4. Secondary Electron Emission .......................................................................... 13
  1.5. Desorption Induced by Electronic Transitions .............................................. 15
    1.5.1. Menzel-Gomer-Redhead Model ............................................................. 16
    1.5.2. Knotek-Feibelman Model ....................................................................... 16
  1.6. Outline of Experiments ................................................................................... 17

Table and Figures ......................................................................................................... 20

CHAPTER TWO: EXPERIMENTAL APPARATUS ................................................. 32
  2.1. Hardware ......................................................................................................... 32
  2.2. Analyzers and Electronics ............................................................................. 35
    2.2.1. Secondary Ion Mass Spectrometry .......................................................... 35
    2.2.2. Secondary Electron Energy Analysis ....................................................... 38

Figures ......................................................................................................................... 40

CHAPTER THREE: EXPERIMENTAL PROCEDURE .......................................... 49
  3.1. Target Preparation ........................................................................................... 49
  3.2. Secondary Ion Yield Measurements .............................................................. 50
1.1. General Introduction

A fast ion striking a solid surface loses its kinetic energy by imparting momentum to target atoms and by exciting target electrons. This mixture of atomic motion, electronic excitation, and projectile implantation can drastically change the properties of the surface by the expulsion of target atoms from the surface ("sputtering") or by the formation of a new compound. Studies of the yield and excitation (or ionization) of the ejected atoms, including their dependences on the characteristics of the projectile and the target surface, can disclose useful information about the surface and the events occurring during the interaction of the projectile with the target. Since the surface of a solid is where much of the solid's interaction with the rest of the world takes place, and ion bombardment of solids occurs both naturally and artificially, this information can be a valuable contribution to various fields of science and technology.

Bombardment-induced modification of a surface can be an important and useful technological and scientific process, or an undesirable side-effect. The implantation of nitrogen into the surface of an artificial hip joint can increase the resistance of the surface to mechanical wear and chemical attack [Pi85], but the impact of plasma ions against the walls of fusion reactors can erode the walls and contaminate the plasma with atoms sputtered from the walls [Be81]. Ion implantation is used for precise doping of semiconductors, but this implantation also damages the solid [Be81, Pi85]. Large organic molecules may be sprayed onto a surface, then sputtered off, allowing
mass analysis of the molecule and its major constituents [To83a, Hu87]. In nature, erosion of surfaces by ion bombardment occurs on the moons of Jupiter, where solid gases are exposed to bombardment by ions trapped in the planet's magnetic field [To82,83a, Jo81].

For studies of sputtering phenomena, sputtered atoms may be post-ionized by lasers for analysis using electrostatic fields and time-of-flight techniques, or they may be collected on a foil for later analysis by Rutherford backscattering [An81, Th87]. The study of the variation of the sputtering yields with such parameters as the energy and angle of incidence of the projectile, as well as the study of the yields of secondary ions, can provide information about the processes which lead to sputtering. The relative ease with which ions can be analyzed has made the study of secondary ions popular, despite the sensitivity of the ionization probabilities to the chemical state of the surface (e.g. oxidation) [Bl79, Wi77,79]. Moreover, secondary ion mass spectrometry (SIMS) is a common, sensitive technique used to study the atomic composition of surfaces as well as the adsorption and bonding of molecules onto surfaces [Be73,75, Wi82a]. The investigation of secondary ions is also important in itself, since the processes of ionization are not fully understood.

The experimental work presented in this dissertation focused on the emission of secondary ions during bombardment of adsorbate-covered metal surfaces by projectile ions having a variety of energies and masses. In particular, we investigated the apparent role played by the bombardment-induced electronic excitation in the emission of positive ions of electronegative adsorbate atoms, as well as the variation of this emission with the target metal and the nature of the
adsorbate-substrate bond. For metals, attention in the past has generally focussed on metal-ion emission produced by momentum transfer during atomic collisions. Also, the study of positive secondary ions of electronegative atoms is fairly recent.

The remainder of this chapter contains a presentation of the basic concepts of sputtering, secondary ion emission, and ion emission stimulated by electron bombardment, in addition to the immediate motivation for and an outline of our experiments. Chapters 2 and 3 contain the details of the experimental apparatus and procedure, while chapter 4 is a discussion of the results of the experiments. Finally, chapter 5 presents conclusions and suggestions for further research.

1.2. Emission of Secondary Ions

Sputtered ions generally are ejected from the surface by an elastic collision with either the incident ion or another target atom. The decay of any excited state of the sputtered particle and the electronic interactions between the particle and the surface then determine the ionization state of the sputtered particle. Therefore, this section first outlines the basic theory of sputtering by atomic collision cascades, then presents various mechanisms that have been proposed for the ionization of sputtered atoms. Sputtering caused by the bombardment-induced electronic excitation of insulating solids will also be discussed.
1.2.1. Sputtering Theory

The basic sputtering theory, set forth by Sigmund, is described in [Si81a]; more recent developments are reviewed in [Si87]. In this theory, Sigmund assumed that the number of target atoms set into motion by the impact of the projectile ion is small enough that moving atoms never collide with one another (linear approximation). However, they do collide with stationary atoms, setting them into motion so that these may in turn collide with other stationary atoms. The resulting cascade of moving target atoms, termed "collision cascade", is shown schematically in fig. 1.1a. This linear cascade, assumed to be isotropic (i.e. the direction of motion after a collision is random), is described by the linear Boltzmann transport equation. Atoms are considered to be sputtered if they cross the surface with kinetic energy greater than the planar surface barrier $U_0$ (typically about 5 eV). Then, solution of the Boltzmann equation for the distribution of moving atoms produces the differential sputtering yield

$$\frac{d^3Y}{dE_1d^2\Omega_1} = S_n(E) \frac{E_1}{(E_1 + U_0)^3} |\cos\theta_1|,$$

where $E$ is the energy of the projectile, $S_n(E)$ its nuclear stopping power, and $E_1$, $\theta_1$, and $d^2\Omega_1$ are the energy, angle of emission with respect to the surface normal, and differential solid angle of the sputtered atom. The parameter $m$ is related to the scattering potential used; often, $m=0$ is used.

There are two features of the sputtering yield that will be pertinent for later discussion. First, the yield is proportional to the nuclear stopping power, shown schematically in fig. 1.1b. The maximum of the
nuclear stopping power occurs when the reduced energy $\varepsilon$ is 0.5, where

$$\varepsilon = \frac{m_2}{m_1 + m_2} \cdot \frac{a}{Z_1 \cdot Z_2 \cdot e^2} \cdot E$$

($Z$ and $m$ are the atomic number and atomic mass; 1 and 2 refer to projectile and target; $E$ is in eV). The screening length $a$ is

$$a = \frac{0.885 \, a_0}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}$$

where $a_0$ is the Bohr radius. The scale of fig. 1.1b can be estimated by reference to table 1.1, which presents the projectile energy and stopping power for the maximum in the nuclear stopping power curve. (Figure 1.1b also shows the electronic stopping power $S_e$, while table 1.1 presents the position of the maximum of $S_e$ and values of $S_e$ at the maxima of $S_n$ and $S_e$.) Second, the energy distribution of sputtered particles is broad (decreases as $E^{-2}$) and has a maximum at low energy.

$$E_{\text{max}} = \frac{U_0}{2(1-m)}.$$  

These two features are verified by experimental results (see [An81] and [Ma84] for compilations of the data).

The sputtering yield formula we used for comparison with our data is the semi-empirical formula proposed by Matsunami et al. [Ma84, Ya83]. This formula takes into account the energy lost by the projectile to electronic excitation of the target and the enhanced
back-scattering of light projectile ions. The sputtering yield is calculated as

\[ Y(E) = \frac{0.42 \cdot \alpha^* \cdot Q \cdot K \cdot s_n(\varepsilon)}{U_S [1 + 0.35 \cdot U_S \cdot s_e(\varepsilon)]} \left(1 - \left(\frac{E_{Th}}{E}\right)^{1/2}\right)^{2.8}. \]

where \( s_n(\varepsilon) \) and \( s_e(\varepsilon) \) are Lindhard's reduced nuclear and electronic stopping powers in terms of the reduced energy \( \varepsilon \) [Li61,63]. \( \alpha^* \), \( Q \), and \( E_{Th} \) are empirical parameters (determined for each beam-target combination), while \( U_S \) is the sublimation energy of the solid (used to approximate the surface barrier \( U_0 \)). In [Ma84], it is shown that this formula provides a good description of experimental sputtering yields.

For metal targets, such as those used in our experiments, bombardment-induced electronic excitations in the bulk decay too quickly to produce appreciable sputtering by electronic processes. This is not necessarily true, however, for targets that are insulators [To83b]. Electronic excitations in frozen gases can survive long enough to migrate to the surface, there to decay and cause sputtering; this mechanism is responsible for some of the sputtering from the moons of Jupiter [To83a, Sc87]. The decay of a defect produced in alkali-halides can result in a replacement sequence which, on reaching the surface, also can produce sputtering [To83b]. That desorption by these mechanisms is produced by electronic excitation rather than by momentum transfer during atomic collision cascades is underscored by the observation that these mechanisms also operate during bombardment of insulating solids by electrons and photons [Br85, To83c]. Finally, Tombrello and Watson [To83d, Wa85] have proposed that the electronic excitation produced by MeV ion
bombardment of dielectric solids (such as UF₄ and Al₂O₃) can change
the lattice electrostatic potential so that lattice atoms are expelled
from the solid.

The sputtering of organic molecules from insulating surfaces also
results from electronic processes. Using fast fission fragments as
projectiles, researchers have found that the sputtering yield is related
to the electronic stopping power; secondary electrons may cause the
sputtering [Hu87, To83a].

1.2.2. Ionization Theory

Models of the ionization of atoms sputtered from metal surfaces
must explain several features of the experimental results (for reviews
of experiment and theory, see [Bl79, Wi77,79,82b, Yu86a,b]). The
secondary ion yields generally follow the sputtering yields as functions
of projectile energy, except for multiply-charged ions produced in
energetic collisions during the early stages of the collision cascade.
The yields of positive ions from a common matrix are proportional to
\( e^{-I/E} \), where \( I \) is the ionization potential of the sputtered atom and \( E \) is
an experimental parameter (the interpretation of which varies from
model to model). Oxidation of the target surface can enhance the
positive ion yield by several orders of magnitude; enhancement of the
negative ion yield is observed when cesium is deposited onto the
target surface. A decrease in the target's work function usually
increases the positive ion yield, and an increase in work function
usually decreases the yield. The sign of the change in yield expected
from the change in work function, however, often is the opposite of
the observed change. In particular, oxidation of the surface can enhance the yield of positive ions while increasing the work function.

We will consider three basic types of ionization models: those invoking energetic collisions, excitation of and electronic interaction with the surface, and breaking of molecular bonds. This discussion will not be a complete review of ionization theory, but rather an overview of concepts which commonly appear in these models.

A sufficiently energetic collision can create a hole in a core electronic level of an atom by Fano-Lichten promotion of that level [Ba72, Fa65]. This mechanism is illustrated in fig. 1.2a, which shows the correlation between the atomic levels for the separated atoms in a collision (between Ar and Cu) and the atomic levels for the "unified" atom (Ag) that is the no-separation limit of the collision. Levels that cross one another can be coupled by the motion of the colliding atoms towards each other (radial coupling) or by their rotation around each other (angular coupling), allowing an electron to be promoted to a higher-energy level (initially empty). The electron initially in the 4f level (derived from the Ar 2p level in fig. 1.2a), which rises steeply and is coupled to many other levels, is particularly prone to promotion. This would leave a hole in the 2p level of the Ar atom (in general, the hole will be on the lighter atom).

According to the kinetic model of ionization proposed by Joyes [Jo73], such a core hole in a sputtered atom will undergo Auger decay, in which a valence electron fills the hole and another electron is ejected (see fig. 1.2b) [Ba82, Be83]. (This Auger decay of atom X is denoted X(CVV), indicating core level C filled by valence electron V, with another valence electron V being emitted.) The sputtered atom
is thus ionized; if several Auger electrons have been emitted in the decay, the atom is multiply ionized. Since this mechanism requires a collision energetic enough for promotion of the 2p level, the ejected ion has fairly high kinetic energy. Also, the ion yield increases with energy rather than following the nuclear stopping power (see [Bl87b,c] for representative experimental results).

According to other models, ionization is produced by the electronic interactions between a sputtered atom and the surface that it is leaving. In the surface excitation model proposed by Williams [Wi79], the electrons near the sputtering event have been excited by the collision cascade; their energy distribution is calculated using Fermi-Dirac statistics. The resonant electron exchange between the surface and the departing particle is assumed to be so strong that the probability that a level in the sputtered atom is empty is equal to the probability that the surface electronic level at the same energy is also empty. The ionization probability is then $e^{-\Delta E/kT_e}$, where $\Delta E$ is the difference between the metal work function and the energy of the atomic level in question when the ion is far enough from the surface that the electron exchange ceases, and $T_e$ is the temperature of the excited electrons.

Several workers [Bl79, Wi79, Sr81] have modelled the interactions between the sputtered atom and the surface by using perturbation theory or tunnelling theory. In general, the motion of the sputtered atom means that the Hamiltonian of the system is time-dependent; this mixes atomic levels with surface levels. The survival probability of an ion at large distances from the surface may be calculated from this perturbation. Figure 1.3a shows schematically what is found for one
such model. As the ion leaves the surface, the electronic interactions with the surface change the widths and energies of its energy levels. The ionization probability is determined by the distance $Z_c$ at which the ionized level crosses the Fermi level of the metal; if $Z_c$ is large enough, electron tunnelling into the ionized level will not occur and the ion will survive. These models (including the surface excitation model) are therefore successful at explaining the dependence of the ionization probability on ionization energy and target work function.

The final model to be discussed is the bond-breaking model, which, based on the Landau-Zener model of molecular dissociation, treats ionization as the result of the break-up of a molecule composed of the sputtered atom and its neighbor on the surface [Yu87]. The level-crossing which occurs during the dissociation is illustrated in fig. 1.3b. The transitions that occur at the crossing-point of the ionic energy curve $M^+ + X^-$ (initial ground-state) with the neutral energy curve $M^0 + X^0$ (dissociated ground-state) determine whether the sputtered particle remains an ion. The ionization probability is then calculated as

$$p^+ = \exp \left( -\frac{2\pi H_{12}^2}{\nu |a|} \right)_{R = R_c},$$

where $H_{12}$ is the transition matrix element, $\nu$ the velocity of the sputtered ion, $R_c$ the position of the crossing, and $|a|$ the absolute value of the difference between the derivatives of the two energy curves as functions of the separation distance $R$. The relevance of the ionization potential, $I$, of the sputtered ion for this model is that $I - A$
(where $A$ is the electron affinity of the neighboring atom) is the separation between the energy curves for large $R$. The bond-breaking model is well-suited for explaining the enhancement of positive ion yields by oxidation of the target, since an oxidized surface is in an ionic state; then the breaking of ionic bonds influences the secondary ion yields more than does the variation of the work function.

1.3. Positive Ions of Electronegative Elements

Recent studies of ion bombardment of electronegative atoms adsorbed onto metal surfaces have found unexpectedly large yields of positive secondary ions from the adsorbates. This contradicts the usual result (discussed in the previous section) that the ionization probability decreases with increasing ionization potential; positive electronegative ions should be easily neutralized. Moreover, the secondary ion energy distributions and the dependence of the ion yields on projectile energy indicate that these ions do not originate from collision cascades. For instance, Williams [Wi81,83] found that the energy distribution of the $F^+$ emitted from fluorinated silicon during bombardment by 8 keV $Ar^+$ did not resemble the energy distribution of the sputtered $Si^+$, but rather that of the $F^+$ emitted during electron bombardment (see fig. 1.4a). Also, the dependence of the $F^+$ yield on incident ion energy resembled that of the $Si(LVV)$ Auger electron yield more than that of the $Si^+$ yield (see fig. 1.4b). The kinetic mechanism of Joyes is ruled out in this case by the low energy of the maximum of the $F^+$ energy distribution. Therefore, Williams proposed that a $Si(LVV)$ Auger electron was creating a core hole in a fluorine atom; the Auger decay of this hole stripped enough electrons
from the fluorine atom to leave it positively ionized. The expulsion of
the F$^+$ from the surface then resulted from the reversal of the
Coulombic forces acting on it.

O'Connor et al. [Bl85, Oc83,85,86a,b] bombarded metal surfaces
with ions having MeV energies. They observed large yields of
electronegative ions which did not follow the metal ion yields as
functions of incident ion energy. An example of their results appears
in fig. 1.5, which also demonstrates that the yields of O$^+$ and Cl$^+$ are as
large as the yields of Y$^+$ for bombardment of yttrium targets.
Reference to fig. 1.1b and table 1.1 shows that the electronic stopping
power is much larger than the nuclear stopping power for the beam
energies used by O'Connor.

The immediate predecessors of our experiments were the
experiments performed by Blauner and Weller [Bl86,87a,b,c], who
studied the emission of O$^+$ from oxidized aluminum and vanadium
surfaces during bombardment by 25-250 keV noble ions. The purpose
of those experiments was to study the secondary ion emission for a
wide range of nuclear and electronic stopping powers. Of particular
interest here is the relative strength of the electronic stopping power
as compared to the nuclear stopping power; the ratios of the former to
the latter, shown in fig. 1.6 for Ne$^+$, Ar$^+$, and Kr$^+$ beams, cover a large
range of values for the projectile energies used.

An example of the dependence of the metal and metal-dimer ion
yields on projectile energy appears in fig. 1.7 (showing the yields of V$^+$
and V$_2^+$ observed by Blauner), along with the sputtering yields
calculated using the formalism of Matsunami et al. (solid lines) [Ma84].
The variation of the metal ion yields with projectile energy are
consistent with ejection produced by collision cascades. The O+ yields from V and Al (shown as functions of beam velocity in fig. 1.8), however, do not follow the sputtering yields but increase linearly with projectile velocity (with the exception of He+ bombardment). Indeed, excluding the data for He+ bombardment, the yields of O+ for the V target are collinear functions of velocity, independent of beam species. Noting the linear dependence of the electronic stopping power S_e on the projectile velocity v, Blauner divided the O+ yields by dS_e/dv, which is projectile-dependent, to remove the dependence on projectile species expected if the emission of O+ depended directly on energy deposited into electronic excitation. The result is shown in fig. 1.9. The Al data for different beams are now closer to falling on a common curve; this is not true for the V data. Nevertheless, because of the linearity in beam velocity of the O+ yields, Blauner proposed that the O+ emission was induced by electronic processes; in particular, desorption stimulated by secondary electrons was suggested, similar to the model of Williams for the ion-induced desorption of F+ (mechanisms of electron-stimulated desorption will be further discussed in section 1.5).

1.4. Secondary Electron Emission

Since secondary electrons appear to be implicated in the ion-bombardment-induced desorption of positive ions of electronegative atoms, a brief discussion of secondary electron emission is in order. Summaries of the experimental results may be found in [Be82, Ha81,88]. For the range of projectile velocities used in our work (2-14 \times 10^7 \text{ cm/s}), the secondary electron yield is proportional to
velocity, as shown by fig. 1.10. In general, the electron yield follows
the electronic stopping power as a function of projectile velocity
(compare fig. 1.10 with fig. 1.1b). The energy distribution peaks at
around 1 eV, then decreases with electron energy \( E \) as \( E^{-n} \), with
\( 1.5 \leq n \leq 3.0 \). The high-energy tail often contains features from the
emission of Auger electrons by the kinetic mechanism discussed in
section 1.2.2 [Ba82, Be82].

The theory of secondary electron emission resembles that of
sputtering by collision cascades [Sc80, Si81b]. The incident ion
produces an electron collision cascade that is described by the linear
Boltzmann equation, with the equation being complicated by the
collisions of moving electrons with (stationary) lattice nuclei. It is,
therefore, not surprising that the theoretical electron yield is found to
be proportional to the electronic stopping power, in agreement with
the experimental results.

Lindhard showed that the electronic stopping power for low
projectile velocities is proportional to the projectile velocity [Li54,61].
Qualitatively, this result may be understood by considering the
reference frame of the moving ion [Li54], in which electrons lose
energy by scattering off of the ion, similar to the mechanism of
electrical resistance in solids. The proportionality of the energy loss
to velocity is then equivalent to Ohm's law (velocity is proportional to
force, hence to energy loss [As76]). Quantitatively, an expression for
the stopping power is found by using quantum-mechanical
perturbation theory to solve for the Fourier transform of the dielectric
constant of the electron gas in the solid; this describes the response
of the electron gas to the moving ion, allowing calculation of the
energy drain on the ion. The result for the electronic stopping power $S_e$ is, in units of eV Å$^2$,

$$S_e = 38.5 \frac{Z_1^{7/6} Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} \sqrt{\frac{E}{m_1}},$$

where $E$ (in keV) and $m_1$ are the energy and atomic mass of the incident ion, and $Z_1$ and $Z_2$ are the projectile and target atomic numbers. Since the square-root factor is proportional to the projectile velocity, the dependence of the stopping power (as a linear function of velocity) on projectile species is contained in the atomic-number factor (henceforth referred to as the "Lindhard factor").

1.5. Desorption Induced by Electronic Transitions

Desorption induced by electronic transitions (DIET) may be produced by bombardment of a solid with electrons (ESD: electron-stimulated desorption) or photons (PSD). ESD will be particularly relevant for our discussion. Because the mass of an electron is small relative to the mass of an atomic nucleus, incident electrons carry relatively little momentum, and the transfer of energy from an electron to a target nucleus is inefficient. Therefore, an incident electron will not produce an atomic collision cascade; desorbed ions must have received their momentum from electronic processes. The desorption of ions from metals also requires a mechanism to allow the ions to escape neutralization by electrons from the surface.
1.5.1. Menzel-Gomer-Redhead Model

The classic model of ESD, proposed by Menzel, Gomer, and Redhead (MGR) [Me64, Re64; see also Go83], is illustrated in fig. 1.11a, which shows potential energy curves for an adsorbate atom A bound to a metal atom M. An excitation of the valence electrons produces a Franck-Condon transition from the ground-state binding curve \( M+A \) to the anti-bonding curve \( M^{-}+A^{+} \). If the departing adsorbate escapes reneutralization, it desorbs as \( A^{+} \). As fig. 1.11a shows, the ion's energy distribution is then the reflection of the ground-state spatial distribution through the excited potential curve. If the ion is reneutralized only after building up sufficient kinetic energy, it escapes as \( A^{0} \); otherwise, the adsorbate atom is recaptured by the surface.

1.5.2. Knotek-Feibelman Model

The MGR model is not adequate to explain the observed ESD of \( O^{+} \) from metal oxides. Since the oxygen is ionized as \( O^{-2} \) in the oxide, a simple valence excitation cannot cause its desorption as \( O^{+} \). Therefore, Knotek and Feibelman (KF) [Fe78, Kn78,79] proposed a mechanism, illustrated in fig. 1.11b, which was the basis for the mechanism proposed by Williams (section 1.3). The desorption begins with the creation by the incident electron (or photon) of a core-hole in the metal atom. In maximally valent oxides, the metal atom has given all of its valence electrons to the oxygen atom. Then the core-hole must be filled by an electron from the oxygen atom (inter-atomic Auger decay), resulting in the ejection of other oxygen electrons and leaving the oxygen atom ionized as \( O^{+} \). With the reversal of the
Coulombic forces, the O+ is repelled from the surface and so desorbs. (A core-hole in an oxygen atom lacks sufficient energy to produce desorption of O+ by an intra-atomic Auger decay mechanism, such as that proposed by Williams for ion-induced F+ desorption.) The desorbing O+ can escape reneutralization since the filling of the holes in its valence shell by metal electrons is slowed by the correlation between the holes [Ci81, Fe81]. Thus, the KF theory predicts O+ desorption from maximally valent systems but not from nonmaximally valent systems.

This prediction is not completely fulfilled, since ESD of O+ is observed for systems that are not maximally valent. For instance, researchers have observed ESD of O+ from NiO [Ge84, Ni81] as well as ESD of F+ from metal fluorides [Wo81]. Indeed, the yield of O+ from TiO2 that has been reduced by ion bombardment is larger than the yield of O+ from undamaged TiO2 [Ku85]. ESD of O+ also is observed from covalent systems, which also are not maximally valent. For instance, CO adsorbs molecularly onto metals such as Ni, with the carbon atom bound directly to the metal and the oxygen atom bound only to the carbon atom; the oxygen atom is thus bound covalently [Ba77, Wo86, Za88]. ESD of O+ is observed, however, from CO adsorbed onto Ni [Ma76, Ra83]. Extensions of the KF theory propose that such desorption can be caused by excitations beyond the simple creation of a core-hole [Ra83].

1.6. Outline of Experiments

We investigated the dependence on projectile velocity of the O+ secondary ion yields, I(O+), during ion bombardment of transition
metal surfaces with separately adsorbed O\(_2\) and CO. The incident ion beams used were 25-250 keV Ne\(^+\), Ar\(^+\), and Kr\(^+\). As fig. 1.6 shows, our beam energies ranged from the regime dominated by nuclear stopping to that where electronic stopping becomes important, providing a good range for determining whether the O\(^+\) emission is better correlated with the nuclear stopping power or with the electronic stopping power.

The adsorbate/substrate combinations used were chosen to provide a variety of initial environments for the oxygen. Two types of oxidized metal surfaces were used. The first group of metals oxidized (Ti, Mo, Nb, and W) is located near V in the periodic table; like V, all these metals can form maximally valent oxides, although researchers disagree on the actual valency of the oxide formed (e.g. [Li74] and [Ca87]). These metals were investigated to determine whether the projectile-independent proportionality of I(O\(^+\)) to projectile velocity, found by Blauner for oxidized V, is a general phenomenon for transition metals or the result of a coincidental cancellation of factors. For these targets, as well as for all other targets, we compared any dependence of I(O\(^+\)) on beam species to the dependences of the electronic stopping power and the secondary electron yields on beam species, to determine the role of electronic excitations or secondary electrons in the emission of O\(^+\).

The other oxidized metal investigated was Ni. As discussed above, some workers have observed ESD of O\(^+\) from NiO, although Ni does not form a maximally valent oxide. Comparison of the dependence of I(O\(^+\)) on projectile velocity for this target with the dependences for bombardment of the maximally valent oxides could then help us
determine the importance of the KF mechanism for ion-induced O⁺ desorption.

We also measured the secondary-electron energy distribution for ion bombardment of oxidized V. If ESD produced by secondary electrons is active during ion bombardment, combining this energy distribution with the known ESD cross-sections as functions of electron energy should allow approximation of the contribution of secondary-electron stimulated desorption to our observed O⁺ yields. If the estimated contribution were to be significantly larger or smaller than the actual yields of O⁺, then the case for secondary-electron stimulated desorption would be weakened. The energy distributions may also indicate whether a significant role is played by Auger electrons in stimulating the desorption of O⁺, as Williams found for the ion-induced desorption of F⁺ from Si.

Finally, we investigated the O⁺ emission induced by ion bombardment of Ni and Pd surfaces with adsorbed CO. For both metals, the adsorption of CO is molecular, with the oxygen atom bound covalently to the carbon atom [Ba77]. The observed ESD of O⁺ from metals with adsorbed CO, in contradiction of the maximal-valency requirement of the KF theory, makes these systems interesting. Also, by comparison of the dependence on projectile velocity of the ion-induced O⁺ yields for these covalent systems with the dependences for the ionic systems, we may determine the effect that the type of bonding of the oxygen has on the O⁺ emission. We also looked for evidence of ion-induced electron-stimulated desorption of CO⁺, since CO⁺ desorption is observed during ESD experiments [Cr83].
Table 1.1

Sample stopping powers and energies of maxima (see fig. 1.1), for Ne+, Ar+, and Kr+ projectiles incident on Ti and W, showing: Energy $E(\varepsilon = 1/2)$ at which nuclear stopping is a maximum, where $\varepsilon$ is the reduced energy; nuclear stopping power $S_n$ and electronic stopping power $S_e$ at the maximum in the nuclear stopping curve; energy $E_{\text{max}}(S_e)$ at which electronic stopping is maximum; maximum electronic stopping power $S_e(E_{\text{max}})$. All stopping powers are given in terms of the energy loss per layer of target material.
<table>
<thead>
<tr>
<th></th>
<th>Nuclear Stopping Power</th>
<th></th>
<th>Electronic Stopping Power</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E(\epsilon = 1/2)$</td>
<td>$S_n(\epsilon = 1/2)$</td>
<td>$S_e(\epsilon = 1/2)$</td>
<td>$E_{\text{max}}(S_e)$</td>
</tr>
<tr>
<td><strong>Titanium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne$^+$:</td>
<td>17 keV</td>
<td>92 eV/layer</td>
<td>38 eV/layer</td>
<td>11 MeV</td>
</tr>
<tr>
<td>Ar$^+$:</td>
<td>43 keV</td>
<td>237 eV/layer</td>
<td>67 eV/layer</td>
<td>47 MeV</td>
</tr>
<tr>
<td>Kr$^+$:</td>
<td>149 keV</td>
<td>588 eV/layer</td>
<td>134 eV/layer</td>
<td>248 MeV</td>
</tr>
<tr>
<td><strong>Tungsten</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne$^+$:</td>
<td>59 keV</td>
<td>83 eV/layer</td>
<td>54 eV/layer</td>
<td>11 MeV</td>
</tr>
<tr>
<td>Ar$^+$:</td>
<td>123 keV</td>
<td>261 eV/layer</td>
<td>177 eV/layer</td>
<td>47 MeV</td>
</tr>
<tr>
<td>Kr$^+$:</td>
<td>318 keV</td>
<td>847 eV/layer</td>
<td>351 eV/layer</td>
<td>248 MeV</td>
</tr>
</tbody>
</table>
Figure 1.1

a) A primary ion strikes a solid surface, producing a collision cascade that can result in the sputtering of target atoms from the first few monolayers of the target (from [Bl87c]).

b) Stopping power \(\frac{dE}{dx}\) of a projectile ion in a solid as a function of projectile energy \(E\). Examples of the locations of and the stopping power at the maxima in the curve are given in table 1.1. For our experiments, the projectile energies were in the nuclear-stopping and Lindhard-Scharff electronic-stopping regimes (from [Sl81a]).
Collision Cascade Model

(a) Sputtered Material

Primary Ion

Target

(b) Log \( |dE/dx| \)

\( E = 1/2 \)

\( v = Z^{2/3} \frac{e^2}{\hbar} \)

\( \log E \)
Figure 1.2

a) Example of a Fano-Lichten correlation diagram, showing the correlation between the atomic levels for colliding atoms of Ar and Cu (right-hand side) and those for the "unified" Ag atom (left-hand side). Solid, dashed, and dotted lines represent $\sigma$, $\pi$, and $\delta$ states (from [Ba72]).

b) Illustration of Auger decay. In the top panel, a core electron of an atom is removed, perhaps through Fano-Lichten promotion. Then, as shown in the middle panel, a valence electron fills the core-hole while another valence electron is emitted. The bottom panel shows the final state: the core-hole has been filled, and two (or more) valence electrons have been removed.
Figure 1.3

a) Change in the energy $E_a$ of an electronic level of an atom (on the right) that is leaving a metal surface (on the left). Because of the electronic interactions between the surface and the atom, $E_a$ and the level width $2\Delta$ both depend on the distance $z$ from the surface. The ionization probability is determined by the distance $z_c$ at which the atomic level crosses the Fermi level of the solid (from [Yu86b]).

b) Molecular potential energy curves, as functions of separation between atoms M and X, for the bond-breaking model of ionization. Curve (ii) is the initial ground-state, in which both atoms are ionized. Curve (i) is the dissociated ground-state, in which both atoms have been neutralized. The interactions between the curves at the crossing point $R_c$ can result in the dissociated state being that for which the atoms are ionized (from [Yu87]).
a) VACUUM LEVEL

\[ E_a(a_0) = -1 \]

\[ \phi \]

\[ E_F \]

\[ z_C \]

\[ 2\Delta(z_C) \]

\[ E_a(\infty) = -I \]

b)

ENERGY

DISTANCE

\[ M^+ + X^- \]

\[ I - A \]

\[ M^0 + X^0 \]

\[ (i) \]

\[ R_C \]

\[ (ii) \]
Figure 1.4

a) Left-hand side: Energy distributions of secondary Si$^+$ and F$^+$ emitted during ion bombardment of fluorinated silicon. Right-hand side: Energy distribution of F$^+$ emitted during electron bombardment of fluorinated silicon (from [Wi81]).

b) Yields of secondary ions and Si(LVV) Auger electrons for 8 keV Ar$^+$ bombardment of fluorinated silicon (from Wi81).
Figure 1.5

Secondary ion yields as functions of projectile energy for MeV ion bombardment of yttrium (from [Oc86b]).
Figure 1.6

Ratio of the electronic stopping power to the nuclear stopping power for 10-1000 keV Ne+, Ar+, and Kr+ primary beams. Stopping powers are calculated using the formalism of Lindhard [Ma84].
Figure 1.7

Yields of metal secondary ions from ion bombardment of clean vanadium surfaces (the labels on the legend are reversed from what they should be). The solid lines represent the sputtering yields calculated according to the formalism of Matsunami et al. and scaled to equal the V+ yields at a beam energy of 200 keV (from [B187c]).
$V^+ \text{ Yields from Clean Vanadium}$

Counts / Incident ion ($10^8$)

Energy (keV)

- Ne
- Ar

$V^+$ $V_2^+$ $V_2^+$
Figure 1.8

a) Yields of secondary O\(^+\) emitted during ion bombardment of oxidized vanadium surfaces, as functions of projectile velocity. For all projectile species except He\(^+\), the data points are collinear, and the extrapolation of the data passes through the origin (from [Bl87c]).

b) Yields of secondary O\(^+\) emitted during ion bombardment of oxidized aluminum surfaces, as functions of projectile velocity (from [Bl87c]).
Vanadium

\[ \text{\(O^+\) Yield (10^7 counts/incident ion)} \]

Velocity (10^8 cm/sec)

Aluminum

\[ \text{\(O^+\) Yield (10^-8 counts/incident ion)} \]

Velocity (10^8 cm/sec)
Figure 1.9
Data from fig. 1.8, divided by $dS_e/dv$, where $S_e$ is Lindhard's electronic stopping power (which is linear in projectile velocity $v$). The solid lines represent empirical electronic stopping powers scaled by the same factors (from [Bl87c]).
Figure 1.10
Secondary electron yield per incident ion, $\gamma$, as a function of projectile velocity $v$ for ion bombardment of metal surfaces. The upper portion of the figure indicates the energies (slanted lines) corresponding to the velocities on the horizontal axis of the lower part of the figure for various projectiles (as labelled on the left side of the upper part of the figure). For our experiments, projectile velocities were in the range $2-14 \times 10^7$ cm/s, which is in the linear regime (from [Be82]).
**Figure 1.11**

a) Illustration of the Menzel-Gomer-Redhead model of electron-stimulated desorption, showing the potential energy curve for an adsorbate A on a metal M before (M + A) and after (M⁻ + A⁺) a Franck-Condon transition of a valence electron. The initial adsorbate wavefunction ψ₁, reflected through the excited potential curve, gives the energy distribution of the desorbing adsorbate, which has minimum kinetic energy $T_{\text{min}}$ (from [Go83]).

b) Illustration of the Knotek-Feibelman mechanism of electron-stimulated desorption from maximally valent metal oxides. A core-hole on the metal atom must be filled by inter-atomic Auger decay involving electrons from the oxygen atom, since the metal atom has no valence electrons. Enough electrons may be lost by the oxygen atom that it becomes positively ionized. Desorption of O⁺ then results from the reversal of the Coulombic forces acting on the oxygen atom (from [Kn79]).
CHAPTER TWO
EXPERIMENTAL APPARATUS

2.1. Hardware

The 300 kV Cockcroft-Walton accelerator used to produce the ion beams for these experiments is shown schematically in fig. 2.1. Neon, argon, or krypton gas was admitted to the hot-cathode ion source through a needle valve and ionized by electrons emitted from the hot filament. The ion source could be operated either with or without the creation of a plasma discharge. In the former case ("lighted" source), the accelerator produced beams with large currents (about 40 μA on target), used for sputter-cleaning the targets. In the latter case ("unlighted" source), the beam currents were 100-1000 times smaller than with the lighted source. Therefore, to avoid significant alteration of the target surface during the secondary ion yield measurements, the primary ion beams used for those measurements were produced by an unlighted source. These beams were more stable, and their currents easier to control, than those produced by a lighted source.

After extraction from the source by the first element of the Einzel lens and acceleration by the potential gradient in the accelerating column, the ion beam was focussed by an electrostatic quadrupole lens (normally needed for a lighted source only) and momentum-analyzed by a 30° bending magnet. For a given magnetic field and accelerator terminal voltage, only those beam ions with a particular value of $\sqrt{m/q}$ ($m = \text{mass}, \ q = \text{charge}$) would be deflected into the ultrahigh vacuum (UHV) beam line. For the heaviest beam ion used, krypton, the analyzing magnet could resolve ions separated in mass by 1 u. The vacuum in the accelerator column and the bending magnet, normally
5-15 ×10⁻⁷ torr, was maintained by an oil diffusion pump with a cold trap.

The UHV beam line is shown in fig. 2.2. The differential pumping necessary to achieve ~10⁻¹⁰ torr in the target chamber with all valves open between the the chamber and the accelerator was achieved by an inline cold trap and two ion pumps. A beam viewer and a Faraday cup at the first UHV pumping station were used to monitor the beam during the tuning of the ion source. A second set of electrostatic quadrupoles supplied most of the beam focussing, while a set of deflection plates rastered the beam to create a uniform beam spot. The size of the beam spot on the target was defined by a collimator located just before the target chamber; a second collimator, slightly larger than the first and electrically biased at -180 V, prevented secondary electrons emitted from the first collimator from hitting the target. The collimators were mounted on a linear manipulator, allowing collimators with various sizes to be inserted into the beam. The first collimator had an 0.25 inch diameter hole used for the sputter-cleaning beams, and an 0.5 mm hole for the beams for the yield measurements.

The target ladder, shown in fig. 2.3a, held the foil targets, as well as a Faraday cup used when positioning the ladder relative to the primary ion beam and measuring beam current. The target ladder was attached to a Huntington PM-600 manipulator, which could move the targets in all three linear dimensions and rotate them through 360°.

Figure 2.3b shows the set-up of the target chamber for the secondary ion yield measurements. The gas bottles were filled with 99.99% pure CO or O₂ (Alfa Products). The gases were admitted to
the target chamber through separate leak valves (Granville-Phillips) that allowed precise control over the partial pressure of the gas in the target chamber. The target ladder was surrounded by a Faraday cage, which could be electrically connected to the target ladder, that captured secondary electrons emitted from the target to improve the measurements of beam current. The Faraday cage had openings for the primary ion beam and the quadrupole mass analyzer.

The mass analysis of the secondary ions was performed by a quadrupole mass analyzer (Uthe Technology Inc., model 100C) that was equipped with an energy pre-filter (Kratos Analytic Instruments). The quadrupole axis was at an angle of 30° with respect to the primary ion beam and perpendicular to the target surface. The position of the target, chosen to maximize the height and resolution of the secondary ion mass peaks, was about 5 cm from the front of the pre-filter.

The set-up of the target chamber for the measurements of the secondary electron energy distribution is shown in fig. 2.3c. Geometrical constraints precluded the use of the Faraday cage in this case. The secondary electrons were energy-analyzed by a cylindrical mirror analyzer (Perkin-Elmer Physical Electronics, PHI 10-155). The analyzer axis was perpendicular to the primary ion beam; the target normal was at an angle of 55° with respect to the beam. The beam spot was large relative to the field of view of the analyzer, so the energy resolution of these measurements was not optimal [0186].

After venting of the target chamber to change targets or analyzers, the chamber was first roughed out by two sorption pumps consecutively, then opened to an ion pump that also contained a titanium sublimator. Baking the chamber for 1.5 days at 120° C
produced a chamber pressure of about $2 \times 10^{-10}$ torr. When the target chamber was open to the accelerator with the ion source unlighted, the pressure remained below $3 \times 10^{-10}$ torr. At this pressure, the time for a monolayer of residual gas to form on the target surface was more than two hours [Ro82].

2.2. Analyzers and Electronics

2.2.1. Secondary Ion Mass Spectrometry

The theory of quadrupole mass analyzers has been presented by Dawson [Da76]. The ideal quadrupole structure, shown in fig. 2.4, consists of four electrodes with hyperbolic cross-sections; for easier construction, electrodes with circular cross-sections are usually used. Adjacent electrodes are oppositely charged, with the voltage difference between adjacent electrodes being an oscillating function of time:

$$\Phi_0 = U - V \cos(\omega t).$$

Then the equations of motion for an ion of mass $m$ and charge $q$ are

$$\frac{d^2x}{dt^2} + \frac{q}{mr_0^2} (U - V \cos(\omega t)) x = 0$$

$$\frac{d^2y}{dt^2} - \frac{q}{mr_0^2} (U - V \cos(\omega t)) y = 0,$$

where $2r_0$ is the separation between opposite electrodes, and $\frac{\omega}{2\pi}$ was $2$ MHz for our quadrupole. These equations are examples of the Mathieu equation.

In the $x$-direction, all ion trajectories would be stable if only the time-independent component of the electric field were present. The
oscillating component of the electric field destabilizes the trajectories of sufficiently light ions, since only light ions can respond quickly enough to the reversals in the direction of the force. In the y-direction, the time-independent component would destabilize all trajectories, but the trajectories of sufficiently light ions are stabilized by the oscillating component. Thus, only those ions light enough to respond to the oscillating component in the y-direction but heavy enough to not respond to the oscillating component in the x-direction will have trajectories stable enough to make it through the analyzer without hitting the electrodes. Examples of "successful" trajectories appear in fig. 2.5. Because the analyzer has finite length, some ions with diverging trajectories, such as those shown in fig. 2.5a and b, can actually pass through the analyzer without hitting the electrodes. Calculations show that the mass resolution of the analyzer is proportional to U/V, while, for a given resolution, m/q for the ions that are allowed through the analyzer is proportional to U (or V). For our experiments, the resolution (full-width at half-maximum) was 0.6 u.

Consideration of fig. 2.5 (particularly parts a and c) shows that the filtering action of the quadrupole increases as the ion experiences more cycles of the oscillating electric field. Thus, the mass of a high-energy ion, which spends little time in the analyzer, is not well resolved. In addition, the background in the mass spectrum can be decreased by preventing negative ions and neutral atoms from entering the quadrupole. Therefore, a cylindrical energy pre-filter, shown in fig. 2.6a, was attached to the entrance of the quadrupole [Bl87c]. With the pre-filter voltages set as shown in fig. 2.6a, ions of
energy 4-6 eV were deflected into the quadrupole; the relative transmission as a function of ion energy is indicated by fig. 2.6b [Bl87c]. A central stop prevented neutral atoms from entering the quadrupole, and the voltages on the pre-filter prevented negative ions from entering. The electrical filters attached to the voltage cables were necessary to eliminate high-frequency electrical pick-up from the quadrupole rods [Bl87c].

A schematic of the electronics for computer control of the quadrupole and for the counting of secondary ions appears in fig. 2.7. The quadrupole rod RF voltages were produced by the RF generator, which was controlled by the UTI 100C quadrupole controller. The m/q value for the ions that were allowed through the spectrometer (0-300 u/e) was proportional to the voltage (0-10 V) at the External Program Input of the controller. This voltage was established by the DAC output of the PDP-11/23+ computer and modified by a biased amplifier to allow coverage of the mass region of interest. The DAC output voltage was proportional to the current channel number of the multi-channel analyzer (Canberra series 40) operated in multichannel scalar mode under computer control to store incoming counts; thus, there was a linear relationship between the secondary ion mass and the number of the MCA channel used to store the counts obtained for that particular mass.

A pulse counted by the MCA ultimately originated with an analyzed ion hitting the channeltron (Galileo); the pulse thus produced was shaped by the fast-timing preamplifier (ORTEC 9305) and amplifier-discriminator (ORTEC 9302). The fast discriminator (ORTEC 417) then converted the pulse to one suitable for input to the MCA.
The computer stepped through programmed ranges of channels ("full" spectrum) or single channels located at the peaks of interest ("spike" spectrum) for a preset number of sweeps, dwelling on each channel for a preset number of interrupts generated by the voltage-to-frequency converter. The frequency of interrupts (0-1 kHz) was proportional to the 0-10 V voltage level sent to the converter by the picoammeter (Keithley 410A). This voltage was in turn proportional to the measured beam current. Thus, counts were accumulated in each channel (or, at each mass) for a pre-determined amount of beam charge incident on the target.

2.2.2. Secondary Electron Energy Analysis

The theory of the cylindrical mirror analyzer (CMA) used to measure the secondary electron energy distributions appears in [Sa67, Za66]. The CMA is shown schematically in fig. 2.8. The electric field between the two coaxial cylindrical electrodes is proportional to 1/r, where r is the radius from the axis of the CMA. The equation of motion for electrons in the CMA is then

\[ m \frac{d^2r}{dt^2} + \frac{U_0}{r} = 0, \]

where

\[ U_0 = \frac{eV_p}{\ln(b/a)}. \]

Here, \( V_p \) is the potential difference between the electrodes, and \( a \) and \( b \) are the radii of the inner and outer electrodes. The energy of the electrons passed by the analyzer is determined by the angle \( \theta_0 \) between the electron's initial velocity and the axis of the analyzer, and by the physical dimensions of the analyzer. For \( \theta_0 \) equal to 42°18.5′,
the first-order angular aberration of the electron trajectories vanishes, and the analyzed electrons are focussed; therefore, CMA's are usually designed to use this angle. Since the resolution (ΔE/E) of the CMA is independent of energy, the measured spectrum is actually EN(E), where N(E) is the true energy spectrum of the electrons [Sa67].

The electronics for controlling the CMA and counting analyzed secondary electrons appear schematically in fig. 2.9. The set-up is essentially the same as that shown previously for secondary ion mass analysis (fig. 2.7). Normally, electron energy spectra (from a CMA) are measured by using lock-in amplification to measure the derivative of the secondary electron current as a function of electron energy. In our case, however, the low primary-ion beam current desired made pulse-counting necessary. Therefore, the electron multiplier, which was connected to the lock-in amplifier, was capacitively coupled to the fast-timing electronics. The voltage level input to the Analog Input of the Auger controller (PHI 500A) was proportional to the outer-cylinder voltage of the CMA. Thus, the channel number of the MCA was linearly related to the energy of the electrons that were allowed by the CMA to reach the electron multiplier.
Figure 2.1

Schematic of the 300 kV Cockcroft-Walton accelerator and analyzing magnet. (From [Bl87c])
WNSL
300 kV Cockcroft-Walton Accelerator

Hot Cathode Ion Source

Accelerating Column

Einzel Lens

Electrostatic Quadrupole Lens

Analyzing Magnet

Differentially Pumped Beam Line
Figure 2.2

The UHV beamline, including the target chamber. The beam enters the cold trap after passing through the analyzing magnet. (From [Bl87c])
UHV Beamline
Figure 2.3

a) Target holder, including a Faraday cup (for measuring beam current) and a quartz viewer. The foil target is held onto the ladder by thin metal strips which are bolted to the ladder. (From [Bl87c])

b) Schematic of the target chamber for secondary ion yield measurements (top view).

c) Schematic of the target chamber for secondary electron energy measurements (top view).
Target Faraday Can
Beam Mass Spectrometer

(a)

CO O₂

(b)

Target Holder
Faraday Cup Quartz Viewer

(c)

Energy Analyzer
Beam Target

CO O₂
Figure 2.4

Electric quadrupole mass analyzer. Opposite electrodes are separated by $2r_0$, while the electric potential between adjacent electrodes is $\Phi_0$. In this figure, the electrodes have the (ideal) hyperbolic cross-section. (From [Da76])
Figure 2.5

Examples of trajectories of ions which pass through the quadrupole mass analyzer. Shown is the amplitude $u$ (in either the $x$-direction or the $y$-direction) as a function of the number of quadrupole voltage rf periods ($\xi/\pi$) experienced by the ion. (From [Da76])
Figure 2.6

a) The energy pre-filter on the quadrupole used for our measurements, shown in cross-section. The pre-filter has cylindrical symmetry. The focus plate voltage was supplied by the UTI controller; the other voltages were supplied by external power supplies.

b) Numbers of Na$^+$ and K$^+$ ions (produced by a heated ion source) passed by the quadrupole and pre-filter for the pre-filter voltages used for our ion yields measurements, as functions of the energy of the ions. (from [Bl87c])
(a) Focus Plate
   Reflecter
   Front Grid
   Central Stop
   Quadrupole

0.1 \mu F
-25 V
0.1 \mu F
2.9 V
-5 V

(b)

V_1 = -5 \text{ v}
V_2 = 2.9 \text{ v}
V_3 = -25 \text{ v}

\text{Na}^+ \text{ counts / 5 sec}
\text{K}^+ \text{ counts / 5 sec}

V_{\text{Source}} (\text{volts})

2.1 \text{ eV}
Figure 2.7

Schematic of the electronics used for control of the quadrupole mass spectrometer and the collection of secondary ions. The cone voltage for the channeltron (-2.8 kV) was supplied by the UTI controller.
Secondary Ions
Target
Quadrupole Rods
Channeltron
-2.8 kV
1 MΩ
50 Ω
Fast-Counting Preamplifier
ORTEC 9305
50 Ω
Amplifier-Discriminator
ORTEC 9302
 Discriminator Output
50 Ω
Fast Discriminator
ORTEC 417
POS Output
92 Ω
ADC in, EXT AMP
Multi-Channel Analyzer
Canberra Series 40
Computer I/O

Filter
0.2 µF
1 kΩ
Amplifier
Integrated Interrupt
DAC Output
I/O Port

PDP 11/23+
Figure 2.8

Schematic of a cylindrical mirror analyzer (in cross-section), showing the focussing property of the CMA about the angle $\theta_0$ (42° 18.5'). Here, $a$ and $b$ are the inner and outer cylinder radii from the axis of the CMA. $V_p$, the voltage on the outer cylinder, is supplied by the Auger controller and determines the energy of the electrons which reach the electron multiplier.
Figure 2.9

Schematic of the electronics for the control of the cylindrical mirror analyzer and the collection of secondary electrons.
3.1. Target Preparation

The targets used in these experiments were 0.127-0.25 mm thick polycrystalline foils (Alfa Products) of Ti, Nb, Mo, W, Ni, and Pd, with the minimum target purity being 99.95%. Before being mounted on the target ladder, the targets were degreased: soaked in warm water and Alconox for 15 minutes, rinsed in tap water, soaked in Freon TF for 15 minutes, rinsed in distilled water, rinsed in isopropyl alcohol, and hot-air dried.

In vacuum, the targets were sputter-cleaned by 200 keV Ar\(^+\) to remove surface contaminants. Before the cleaning, full secondary-ion mass spectra of the initial targets were taken for calibration of the mass-scale of the MCA and for comparison to full spectra taken after the sputter-cleaning. A mass spectrum of an initial target of titanium appears in fig. 3.1a, showing the presence of Na, K, and TiO on the target surface. The 40-60 μA ion beams used for sputter-cleaning were rastered and collimated to form a 1 cm\(^2\) beam spot. The total beam charge incident on the target during the cleaning was 0.4-1.0 Coulomb, which was sufficient to remove 2-15 \times 10^3 \text{ monolayers} of target material (estimated from the semi-empirical sputtering yield found in [Ma84]). The sputter-cleaning was continued until secondary-ion mass spectra showed that further cleaning would not significantly reduce the level of surface contaminants. A mass spectrum of clean titanium appears in fig. 3.1b, showing the elimination of Na\(^+\) and K\(^+\), the reduction of the amount of TiO\(^+\), and the observation of Ti\(_2^+\) (which indicates a clean target surface [Bl87a]).
After the completion of the sputter-cleaning, the targets were exposed to the adsorbate gas at a pressure of $1 \times 10^{-6}$ torr for an amount of time chosen to allow saturation of the surface (determined by alternating adsorption with the taking of mass spectra). For O$_2$ adsorption, this time was 1000 s [Bl87c], while for CO adsorption it was 2000 s. Throughout the secondary ion yield measurements, a residual pressure of $5 \times 10^{-8}$ torr of the adsorbate gas was maintained in the target chamber. This residual gas could then adsorb onto the surface during the measurements to replace sputtered adsorbate atoms or molecules. At the start of each day, the target was again sputter-cleaned (for about 30 minutes), and the adsorption was repeated.

After the adsorption, another full mass spectrum was taken for each target. Sample mass spectra appear in fig. 3.2 for O$_2$ adsorbed onto Ti (denoted O/Ti) and for CO adsorbed onto Ni (CO/Ni). For O$_2$ adsorption, the spectra generally consisted of $M^+$ and $MO^+$, with some $O^+$, $Na^+$, $Fe^+$, and complex metal-oxide ions. For CO adsorption, the spectra consisted of $M^+$, $O^+$, $Na^+$, and $MCO^+$, in addition to a barely measurable amount of $CO^+$. Particularly important is the absence of $MO^+$ or $MC^+$ in the mass spectra for CO adsorption, which shows that the adsorption is indeed molecular rather than dissociative [Ba77].

3.2. Secondary Ion Yield Measurements

3.2.1. Procedure

The procedure for the secondary ion yield measurements was essentially that used by Blauner and Weller [Bl87c]. After the target surfaces were prepared by sputter-cleaning and adsorption, the
secondary ion yields were measured during bombardment of the targets by beams of 25-250 keV Ne+, Ar+, and Kr+. The primary ion beams, rastered and collimated to form a beam spot of 0.09 cm², were incident on the target at an angle of 30° from the target normal. Significant damage to the target surface during the yield measurements was avoided by the use of low beam currents (0.5-1.0 nA) for short times (5 nC incident charge per MCA channel, or about 5-7 minutes total per spectrum). The amount of target material removed during the measurement of a mass spectrum was less than 0.02 monolayer [Ma84], qualifying these measurements as static SIMS [Be73].

The secondary ion yield measurements were repeated several times for each beam energy (not consecutively). Measurements using 200 keV Ar+ beams were made throughout each run to verify the constancy of the surface and to provide the basis for normalizing the data for day-to-day variations in the experimental conditions.

The mass spectra taken for the yield measurements consisted of the counts measured at a single channel corresponding to the peak of each interesting mass, as determined from the full mass spectra. (For the measurements of the O+ yields from bombardment of CO/Ni and CO/Pd, 3 channels were used.) Other, off-peak channels were included in each sweep to monitor the background (found to be negligible). Each spectrum included 10-20 sweeps of 10-20 channels; the number of sweeps was chosen so that the statistical uncertainty of the number of counts in the O+ peak was 1-2%.
3.2.2. Corrections for Systematic Errors

The measured secondary ion yields were corrected for three sources of systematic error in the measurement of the incident beam current. Since counts were collected for a specified amount of beam charge incident on the target, incorrect current measurements resulted in systematic errors in the number of counts per incident ion.

Two of the sources of error were a background or leakage current $I_c$ (about -10 pA) from the Faraday cage, and an increase in measured beam current that was proportional to the increase in the quadrupole rod voltage (about 5-10 pA maximum). The latter error varied with MCA channel number; letting $I_v$ be the increase observed for the highest channel number used for the mass spectrum, then the increase for a particular channel was $ch \cdot I_v$, where $ch$ was the ratio of the particular channel number to the highest channel number. These two sources of error were measured immediately before and after the collection of each mass spectrum.

The third source of systematic error resulted from the escape of secondary electrons to the quadrupole pre-filter. These electrons were not captured by the Faraday cage and thus constituted a contribution $I_p$ to the measured beam current. This error was corrected for by making separate current measurements which included the pre-filter (along with the target and the Faraday cage) in the current-integration circuit. Measurements of the beam current with the Faraday cup mounted on the target ladder verified the accuracy of these measurements. Therefore, it was assumed that the beam current thus measured was the actual beam current $I$. Moreover, it was assumed that the fraction of secondary electrons hitting the
pre-filter, proportional to $I_p/I$, was a constant for a given combination of beam species, beam energy, and target metal, and that the $I_p/I$ thus measured could, therefore, be used in the correction of the secondary ion yield data.

The current $I_n$ during collection of counts into a particular channel was

$$I_n = I + I_p + I_c + ch \cdot I_v .$$

Therefore, the correction factor $k$ for the secondary ion yield per incident beam ion was

$$k = \frac{I_n}{I} .$$

(If the measured beam current $I_n$ were larger than the actual beam current $I$, then counts were accumulated for too short of a time; thus, the yield per incident ion was increased to compensate.) In practice, the currents recorded for a given mass spectrum were $I_c, I_v,$ and the beam current $I_m$ measured at the start of each spectrum ($ch = 0)$:

$$I_m = I + I_p + I_c .$$

Thus, the correction factor was actually calculated as

$$k = \frac{I_m + ch \cdot I_v}{I_m - I_c} \cdot \frac{I + I_p}{I} .$$

3.3. Secondary Electron Yields and Energy Distributions

The secondary electron yields were estimated for each run by also measuring the current $I_t$ for the target alone (without the Faraday cage in the circuit to collect secondary electrons). Then the secondary electron yield per incident ion was
\[ \gamma_e = \frac{I_t}{I} - 1. \]

(These yields were also corrected for the sources of systematic error discussed above.) The secondary electron yields were measured as functions of beam velocity for comparison with the yields of secondary O\(^{+}\) ions.

Secondary electron energy distributions were measured with the cylindrical mirror analyzer (CMA); beams of 50-200 keV Ar\(^{+}\) were used as projectiles, with O/V as the target. Full spectra were taken, covering the energy range 0-2000 eV, with several sweeps per spectrum. The focusing properties of a CMA are such that the energy resolution \( \Delta E/E \) is independent of electron energy \( E \) \cite{Sa67}, so that the range \( \Delta E \) of electron energies contributing to the counts in a particular MCA channel increased with electron energy. Therefore, the data were divided by the secondary-electron energy to produce the final spectra presented in the following chapter.
Figure 3.1

a) Full secondary-ion mass spectrum (mass range 0-200 u) for 200 keV Ar\(^+\) bombarding a Ti target as initially put into the target chamber (after degreasing), for total incident charge of 0.6 nC per MCA channel.

b) Full secondary-ion mass spectrum (0-200 u) for 200 keV Ar\(^+\) bombarding sputter-cleaned Ti (about 1400 monolayers removed during the cleaning), for total incident charge of 1.0 nC per MCA channel.
a) Initial Ti

![Graph of initial titanium concentrations with peaks for Na⁺, K⁺, Ti⁺, and TiO⁺.]

b) Sputter-cleaned Ti

![Graph of sputter-cleaned titanium concentrations with peaks for Ti⁺ and Ti₂⁺.]

Channel Number

Counts
Figure 3.2

a) Full secondary-ion mass spectrum (mass range 0-200 u) for 200 keV Ar$^+$ bombarding Ti after sputter-cleaning followed by exposure to 1000 L of O$_2$ (1 L = 10$^{-6}$ torr·s); total incident charge was 0.2 nC per MCA channel.

b) Full secondary-ion mass spectrum (0-200 u) for 200 keV Ar$^+$ bombarding Ni after sputter-cleaning followed by exposure to 2000 L of CO; total incident charge was 0.1 nC per MCA channel.
Figure 3.2

a) Full secondary-ion mass spectrum (mass range 0-200 u) for 200 keV Ar\(^+\) bombarding Ti after sputter-cleaning followed by exposure to 1000 L of O\(_2\) (1 L = 10\(^{-6}\) torr-s); total incident charge was 0.2 nC per MCA channel.

b) Full secondary-ion mass spectrum (0-200 u) for 200 keV Ar\(^+\) bombarding Ni after sputter-cleaning followed by exposure to 2000 L of CO; total incident charge was 0.1 nC per MCA channel.
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1: O₂ Adsorption onto Ti, Nb, Mo, and W

As an example of the dependence of the metal secondary ion yields on the energy of the incident beam, fig. 4.1 shows the yields of Mo⁺ from Ne⁺, Ar⁺, and Kr⁺ bombardment of O/Mo. (All secondary ion yields presented in this chapter have been corrected for the systematic errors discussed in section 3.2.) The dependence on beam energy of all other metal and metal-oxide ion yields, for all targets studied, resembled that of Mo⁺. Figure 4.1 also shows the total Mo sputtering yields, calculated using the semi-empirical formalism of Matsunami et al. [Ma84] and arbitrarily scaled to equal the measured secondary ion yields at 200 keV. The empirical scaling factors S, tabulated in table 4.1 for all adsorbate/substrate systems studied, are the products of two unmeasured quantities:

\[ S = T \cdot I^+ , \]

where the transmission factor T includes the angular acceptance and transmission of the mass spectrometer, as well as the efficiency of the channeltron, while I⁺ is the ionization probability of a sputtered atom. Benninghoven [Be75] found I⁺ to be 0.4 for Ti⁺ and 0.035 for W⁺; when these numbers are combined with the decrease in the transmission of a quadrupole mass spectrometer with increasing ion mass [Da76, Ut79], T is found to be of the order 10⁻⁶-10⁻⁵.

The scaling factors decrease slightly from Ne⁺ to Kr⁺; this decrease could result from the combination of the choice of 200 keV as the standard energy and the difference between the beam-energy dependence of the secondary ion yields and that of the sputtering
yields. The difference in the dependence on beam energy between the emission of secondary ions and sputtered atoms could indicate that, for the lower beam energies and the heavier beam ions, the collision cascade was too dense to be adequately described by the linear collision cascade theory; this would have resulted in a secondary ion yield that was larger than that predicted by the linear theory [Si81a].

Figures 4.2 and 4.3 show the yields of secondary O$^+$ ions emitted during ion bombardment of oxidized Ti, Nb, Mo, and W targets. The O$^+$ yields increase linearly with beam velocity; the parameters from linear fits to the data are presented in table 4.2. Comparison of these figures with fig. 4.1 shows that for these targets there is a clear difference between the dependence of the metal ion yields on beam energy and that of the oxygen ion yields; this result is consistent with the results obtained by Blauner and Weller for bombardment of oxidized Al and V [Bl87a,b,c].

Figure 4.4 shows the yields of secondary electrons emitted during ion bombardment of O/Mo and CO/Ni. These yields also increase linearly with beam velocity, as expected from the experimental and theoretical results discussed in section 1.4. The parameters from linear fits to the secondary electron yields as functions of beam velocity appear in table 4.2. The discussion in section 4.1.1 will center on comparisons of the beam-velocity dependence of the O$^+$ yields with that of the secondary electron yields and that of the electronic stopping power; the dependences of the latter two are expected to be similar. If a connection exists between electronic excitation and O$^+$ emission [Bl87a], one might expect a correlation between the O$^+$
yields and either the secondary electron yields or the electronic stopping power (or both).

### 4.1.1. O⁺ Emission

As shown in fig. 4.2 and table 4.2, the O⁺ yields from ion bombardment of O/Ti and O/Nb are collinear for all beams and are strictly proportional to beam velocity, with the exception of the yields from Ne⁺ bombardment of O/Nb. This result agrees with the result of Blauner and Weller for ion bombardment of O/V [Bl87a]. Therefore, the lack of explicit dependence on beam species probably does not result from a coincidental cancellation of factors or a peculiarity of any of these systems. For Ne⁺ bombardment of O/Nb, the y-intercept found from a linear fit to the data is significantly different from zero; this apparent offset of the O⁺ yields will be discussed further in section 4.1.2.

The linear dependence of the O⁺ yields on beam velocity for ion bombardment of O/V, O/Ti, and O/Nb suggests that electronic processes are active. However, one might then expect an explicit dependence on beam species, since the secondary electron yields and the electronic stopping power depend on beam species as well as on beam velocity. For instance, the slope of the secondary electron yields as a function of beam velocity for bombardment of O/Ti increases by a factor of 3 from Ne⁺ to Kr⁺; as expected from the discussion in section 1.4, this increase is similar to that of the Lindhard stopping power factor (0.332 for Ne⁺, 0.805 for Kr⁺). This increase, however, is not reflected in the O⁺ yields from bombardment of O/Ti. Also, if the O⁺ yields scale as the electronic excitation, then division of the yields by
the Lindhard stopping power factor should cause the data for different beams to fall on a common line. Clearly, this will not occur for O/Tl; fig. 4.5 shows that this scaling also does not occur for O/Nb. We can also compare the O\(^+\) yields directly to the secondary electron yields by computing the ratios of the slopes determined by linear fits to the two sets of data. Although these ratios are consistent with one another for bombardment of O/Nb, this consistency is not as compelling as that found for O/Mo (discussed below) and results, to some extent, from the large statistical uncertainty in the ratios.

Treating Ne\(^+\) bombardment of O/Nb as a special case, it therefore seems reasonable to group O/Nb, O/Tl, and O/V together as systems for which the O\(^+\) yields are proportional to beam velocity, with no additional dependence on beam species. This suggests that, for these targets, the O\(^+\) emission does not arise from a mechanism, such as desorption induced by secondary electrons, which depends in a simple manner on the total energy deposited into electronic excitation. (It must be noted, however, that this simple argument assumes that the fraction of secondary electrons with sufficient energy to initiate desorption is a constant for all beam species and beam velocities.) Moreover, in section 4.1.3 it will be shown that the magnitude of the O\(^+\) yields is not consistent with desorption induced by secondary electrons.

The literature on the oxidation of transition metal surfaces contains few determinations of the stoichiometry of the oxide formed for exposures similar to those used in this study. Moreover, those determinations have often produced conflicting results; for instance, the oxide formed on Ti has been found to be TiO by one group [Ro84]
and TiO₂ by another [Ca87]. Therefore, since we did not attempt to characterize our oxides, it cannot be certain that the oxides were, in fact, maximally valent. Such a characterization could shed light on the mechanism responsible for the dependence of the O⁺ yields on beam velocity for O/Nb, O/Ti, and O/V. A finding that the oxides were not maximally valent would relate our studies to those of ESD of O⁺ from beam-reduced TiO₂ (discussed in section 1.5.2).

Figure 4.3, along with consideration of the linear fit parameters presented in table 4.2, demonstrates that the O⁺ yields from O/Mo and O/W, as functions of beam velocity, do depend explicitly on beam species. This dependence is compared with that of the electronic stopping power in fig. 4.6, which shows the O⁺ yields divided by the Lindhard factor, and in table 4.2, which presents the slopes of the scaled O⁺ yields and the ratios of the O⁺ slopes to the secondary electron slopes. For both targets, the scaled yields coincide for the Ar⁺ and Kr⁺ beams. Although the scaled yields for Ne⁺ bombardment of O/Mo are higher than those for the Ar⁺ and Kr⁺ beams, the scaled slopes and the ratios of the slopes show that the O⁺ yields for Ne⁺ bombardment of O/Mo do scale with the electronic excitation. This is not the case for Ne⁺ bombardment of O/W; moreover, here the Ne⁺ data are offset by a relatively small amount compared to that found for O/Mo and O/Nb, although the offset is still significantly different from zero.

Therefore, for all beam species bombarding O/Mo and O/W, with the exception of Ne⁺ bombarding O/W, the O⁺ yields have a component whose dependence on beam species is consistent with the suggestion [Bl87a] that the O⁺ emission is caused by secondary electrons or by
some other form of electronic excitation. This is in contrast to the results for O/V, O/Tl, and O/Nb. Figure 4.7 shows the relevant portion of the periodic table and summarizes the behavior of the O+ yields. Apparently, the details of the O+ emission from a metal surface are influenced by some property that varies with the column of the periodic table of the metal substrate, such as the electronic structure of the metal or the metal oxide. Given the uncertainty about the valency of the oxides, it is possible that the relevant property could be whether a maximally valent oxide is actually formed.

4.1.2. Ne+ Bombardment

For Ne+ bombardment of O/Nb, O/Mo, and O/W, the O+ yields are offset from being strictly proportional to beam velocity; this is in contrast to the behavior of the O+ yields for all other beam/target combinations discussed thus far. Systematic error seems to be an unlikely explanation of the offsets, since, although they were reproducible, they were not observed for Ne+ bombardment of O/V and O/Tl (if there were a problem associated with the use of Ne+ beams, it should have resulted in offsets for all targets). If the linear fits to the O+ yields hold true for lower beam velocities than used in this study, with an extrapolated nonzero yield at zero beam velocity, then the additional emission of O+ may be related to the potential energy of the incident Ne+. If, however, the O+ yields go to zero for the lower beam velocities, as suggested by the data for the lowest beam energy used here, then a kinetic mechanism (similar to that discussed in section 1.2.2 for the emission of multiply-charged metal...
ions) could be implicated, e.g. one invoking a direct collision between a backscattered Ne+ ion and an adsorbed oxygen atom.

The secondary electron yields during Ne+ bombardment are also offset, as shown in table 4.2. Following the hypothesis that secondary electrons can cause O+ emission, it is reasonable to look for a connection between the O+ offset and the secondary electron offset. This connection could take one of two forms. First, the Ne+ bombardment could have produced an additional source of secondary electrons whose yield did not increase linearly with the beam velocity, either by neutralization of the Ne+ or by some kinetic mechanism such as electron promotion (section 1.2.2). These additional electrons then could have caused the O+ emission by the same ESD mechanism responsible for the velocity-proportional emission. In this case, one would expect the offsets of the O+ yields for different targets to scale as the O+ yield per secondary electron found for velocity-proportional emission; that is,

\[
\frac{b(O^+)}{b(e^-)} = \frac{m(O^+)}{m(e^-)},
\]

where \(m\) and \(b\) are the slope and y-intercept. However, the ratio of the left-hand side to the right-hand side is not consistent with unity for any target (4.7 ± 1.7 for Nb, 2.6 ± 0.9 for Mo, and 2.7 ± 0.6 for W). (It is conceivable, however, that the additional electrons had such an energy distribution that they were more efficient at producing O+ desorption than the bulk of the secondary electrons.)

The second type of connection between the O+ offset and the secondary electron offset would be that the additional secondary electrons were an incidental by-product of some other process that
produced the extra O⁺ emission. For instance, the O⁺ emission could have been produced by a kinetic mechanism similar to that discussed in section 1.2.2 for the emission of multiply charged metal ions, or by Auger neutralization of the incident Ne⁺ by an oxygen valence electron, leading to the stripping of the other valence electrons. In the former case, one would expect the O⁺ emission to go to zero for zero beam velocity, while for the latter case that is not necessarily true. In either case, the emitted Auger electrons would be the observed additional secondary electrons.

If the additional electrons were the result of, rather than the cause of, the additional emission of O⁺, the ratios of the O⁺ offset to the secondary electron offset should be independent of the target. These ratios are (in units of 10⁻⁷ O⁺/electron) 2.7 ± 0.8 for Nb, 2.6 ± 0.8 for Mo, and 0.6 ± 0.1 for W. The apparent consistency between Nb and Mo may be encouraging. Further study of the low-energy behavior of the O⁺ yields during Ne⁺ bombardment is clearly needed.

Any speculation about the existence of a mechanism for O⁺ emission that is unique to Ne⁺ bombardment must be tempered by consideration of the results from bombardment of O/Ti and O/V. Although the secondary electron yields are offset for both Ne⁺ and Ar⁺ bombardment of O/Ti, the O⁺ yields are not offset for any beam. Blauner’s results for bombardment of O/V also show no signs of an offset of the O⁺ yields [B187a,c]. Therefore, the suggestion that Ne⁺ bombardment produces an additional source of secondary electrons which then cause O⁺ emission is not supported, since for O/Ti the additional secondary electrons were observed, but the additional O⁺ emission was not observed. Also, one would expect that a mechanism
for O+ emission invoking a direct interaction between the incident ion and the oxygen atom would operate for V and Ti as well as for Nb, Mo, and W.

4.1.3. Secondary Electron Energy Distributions

Figure 4.8 shows the secondary electron energy distribution measured for 200 keV Ar+ bombardment of O/V. Similar distributions were measured for incident Ar+ beams having other energies. The broad feature at around 200 eV is a Doppler-broadened Ar Auger peak [Be82].

If secondary electrons were causing the emission of O+ by electron-stimulated desorption, then the cross-section \( \sigma(O^+) \) for ion-induced emission should be

\[
\sigma(O^+) = \int Y_e(E_e) \sigma_{ESD}(E_e) \, dE_e ,
\]

where \( Y_e(E_e) \) is the secondary electron energy distribution and \( \sigma_{ESD}(E_e) \) is the cross-section for ESD of O+ by an electron with energy \( E_e \). The electron energy distribution in fig. 4.8 was used to estimate the O+ yields expected from ESD induced by secondary electrons. An example of the dependence of the ESD cross-section for the emission of O+ on the electron energy is shown in fig. 4.9 [Fe78]. For the simple calculations in this section, the ESD yield per electron, \( Y_{ESD} \), was approximated as increasing linearly from threshold at 30 eV to a maximum, \( Y_{\text{max}} \), at 90 eV, remaining at \( Y_{\text{max}} \) for larger electron energies.

The expected yield of O+ desorbed by secondary electrons was then calculated as
both summations were over electron energy. Here, \( \gamma_e \) is the total secondary electron yield determined from the ion beam current measurements, and \( Y_e \) is the secondary electron distribution shown in fig. 4.8. Although the transmission of the mass spectrometer, \( T \), was estimated to be of the order \( 10^{-5} \) for Ti\(^{+} \) (section 4.1), the Ti\(^{+} \) energy distribution has a maximum at about 10 eV [Sn78], compared to the 4-6 eV range of the energy pre-filter used for our measurements. In contrast, approximating the energy distribution of the emitted O\(^{+} \) by a Gaussian distribution, with the width and the position of the maximum being those found by Weng for ESD from O/Ti (fig. 4.10) [We81], shows that about one-half of the O\(^{+} \) would have energies within the range of the pre-filter. It would be expected, therefore, that \( T \) was actually better than \( 10^{-5} \) for the O\(^{+} \) ions; for this calculation, \( T \) was estimated as \( 10^{-4} \).

The result of the calculation was that the expected yield of O\(^{+} \) from secondary-electron-induced desorption during 200 keV Ar\(^{+} \) bombardment of O/V would be

\[
Y(O^{+}) = \gamma_e \cdot T \cdot \frac{\Sigma (Y_{ESD} \cdot Y_e)}{\Sigma Y_e}
\]

with \( Y_{max} \) being typically of the order \( 10^{-6}-10^{-5} \) O\(^{+} \)/electron [Kn84, Re64], then the expected O\(^{+} \) yield would be about \( 10^{-10} \) O\(^{+} \)/ion. This is much smaller than the observed O\(^{+} \) yield from O/V, about \( 2.5 \times 10^{-7} \) O\(^{+} \)/ion [Bl87a], by a factor of 2500. Although this calculation was crude and the conditions for measuring \( Y_e \) were not optimal, the hypothesis of secondary-electron-induced emission of O\(^{+} \) appears to be inconsistent with the magnitude of the observed O\(^{+} \) yields. It must be
noted, however, that this calculation does not apply to emission produced by other forms of electronic excitation. The calculation would be improved by using the same pre-filter and quadrupole mass spectrometer for both ion- and electron-bombardment experiments, thereby eliminating $T$ from the calculations and obtaining an accurate value of $Y_{\text{max}}$ for the specific target surfaces studied. More accurate measurements of $Y_e(E_e)$ for these targets are also needed.

The yield and the energy of Auger electrons produced by ion bombardment depend on the beam-target combination [Ba82, Be82]. Therefore, it was of interest to estimate the contribution of the Ar Auger electrons to the calculated $O^+$ yield from secondary electrons in order to determine whether part of the measured variation of the $O^+$ yield with beam species could have resulted from variations in the Auger electron yield. The background of secondary electrons (shown in fig. 4.8) was estimated from the energy distribution on both sides of the Auger feature and subtracted from the electron energy distribution, leaving only the Ar Auger feature. This feature was used for the energy distribution $Y_e$ in a second set of calculations performed in the manner described above. It was found that the fraction of the calculated $O^+$ yield that was caused by Ar Auger electrons ranged from 6% for 50 keV beams to 15% for 200 keV beams. Since this fraction was less than or equal to the scatter in the $O^+$ yield data, it is difficult to ascribe any significant effect to it for $Ar^+$ beams. However, similar measurements and calculations should be made for $Ne^+$ and $Kr^+$ beams, since the yield induced by Auger electrons could be greater for those beams, or their Auger electrons could be more effective at producing desorption.
Since the energy pre-filter on the quadrupole mass spectrometer sampled only a narrow range of O+ energies, a change in the O+ energy distribution with beam energy or beam species could have produced systematic errors in the variations of the O+ yields with beam velocity and beam species. Figure 4.11 shows that the shape of the energy distribution of the secondary electrons depends on beam energy [Be82], while fig. 4.10 shows that the shape and position of the O+ energy distribution (for ESD) can change with electron energy [We81]. Therefore, a change in the O+ energy distribution with ion beam velocity and beam species is possible. Calculations combining Weng's O+ energy distribution [We81] with the measured secondary electron energy distributions for several ion beam energies showed that the fraction of the emitted O+ ions that had energies in the energy range of the pre-filter was independent of beam energy for Ar+ bombardment of O/V. It was desirable, however, to calculate whether the limited energy range of the pre-filter was introducing systematic error for other beam-target combinations. Therefore, assuming that the tail of the secondary electron energy distribution decreased with increasing electron energy E as E^{-n} for 1.5 \leq n \leq 3.0 [Ha87], we calculated the effect of variations of n on the estimated O+ yield. (The assumed behavior of the ESD cross-section was the same as that used above.) The maximum change in the calculated O+ yield was less than 4% over this range of n. Given that the actual range of n may not have been this large for our experiments, this result sets an upper limit on the systematic error introduced by the energy range of the pre-filter. Since the scatter in the O+ yield data was about 15%, the systematic error introduced by the pre-filter was negligible.
4.2. O/Ni Targets

Figure 4.12 shows the yields of O+ and Ni+ from ion bombardment of oxidized nickel (the O+ yields have been scaled to equal the Ni+ yields at 200 keV). Although the O+ yields are not exactly proportional to the Ni+ yields as a function of beam velocity, the dependences of the yields on beam velocity are very similar; the yields certainly do not increase linearly with increasing beam velocity, unlike those for the other oxidized targets discussed thus far. Therefore, it appears that the emission of O+ during ion bombardment of O/Ni results from collision cascades rather than from electronic processes.

This result, however, may not be inconsistent with the observation of ESD of O+ from O/Ni [Ge84, Ma76, Ni81]. Gerritsen [Ge84] found the total ESD yield of oxygen atoms from O/Ni to be about 2×10⁻⁸ atoms/electron. Since, typically, less than 10% of the total ESD yield is ionized [Kn84], this implies an O+ yield of less than 2×10⁻⁹ O+/electron, which is a factor of 10⁻³ smaller than the ESD yields of O+ from maximally valent metal oxides. It would be expected, therefore, that any electronically-induced emission of O+ during ion bombardment of O/Ni would be smaller than that from O/Ti by a similar factor. Comparison of the observed O+ from ion bombardment of the two targets, however, shows that the yields from O/Ni (presumably from collision cascades) are smaller than those from O/Ti by a factor of only 10⁻². This crude calculation suggests that, for ion bombardment of O/Ni, the yields of any O+ desorption induced by electronic processes may be too small to be observable above the O+ emission from collision cascades.
4.3. CO Adsorption

4.3.1. CO+ Emission

Figure 4.13a shows the yields of CO+ and Ni+ from Ar+ bombardment of CO/Ni, with the CO+ yields scaled to equal the Ni+ yields at 200 keV. Figure 4.13b shows the equivalent data for Ar+ bombardment of CO/Pd. The similarity between the behavior of the CO+ yields as functions of beam velocity and that of the metal ion yields shows that the emission of CO+ from CO/Ni and CO/Pd is probably produced by collision cascades. Although Craig has observed ESD of CO+ from CO/Ni [Cr83], he does not present the absolute magnitudes of the ion yields, so that the expected yield of CO+ emission induced by secondary electrons cannot be estimated. Craig does report, however, that the CO+ yield was 0.4 times the O+ yield [Cr83], while our ion-induced CO+ yield was only 0.1 times our ion-induced O+ yield. It may be significant that our targets were exposed to 2000 L (1 L = 10^-6 torr × s) of CO, in contrast to the 3 L exposure used by Craig. Also, Craig used 400 eV electrons in his experiments; fig. 4.8 shows that very few of the secondary electrons emitted during ion bombardment would have such an energy. It is possible, therefore, that, for Craig's electrons, the ratio of the ESD cross-section for CO+ emission to the cross-section for O+ emission was different from the ratio for the secondary electrons emitted during ion bombardment, which would explain the discrepancy in the ratio of the CO+ yields to the O+ yields between our experiments and Craig's experiments.
4.3.2. Ni$^+$ Emission

Figure 4.14 shows the yields of Ni$^+$ for Ar$^+$ bombardment of O/Ni and CO/Ni; the yields for O$_2$ adsorption have been scaled to equal those for CO adsorption at 200 keV. The dependence of the Ni$^+$ yields on beam energy is similar for the two adsorbates, with the yields being approximately proportional to the sputtering yield. The measured Ni$^+$ yields from the CO-adsorbed target are larger than those from the O$_2$-adsorbed target by more than an order of magnitude (see table 4.1). This extra enhancement of the Ni$^+$ yield by adsorption of CO has been observed previously by Winograd [Wi82c]. Since the Ni-CO bond is not highly ionic [Wi82b, Za88], this enhancement cannot be easily explained by the bond-breaking model often used to explain the enhancement of metal ion yields by O$_2$ adsorption (section 1.2.2). Clearly, the effects of adsorption on secondary ion emission are not fully understood.

4.3.3. O$^+$ Emission

The yields of O$^+$ from ion bombardment of CO/Ni and CO/Pd are shown in fig. 4.15. In some respects, the data resemble those for the oxidized targets, excluding O/Ni; the yields for CO adsorption certainly do not follow the sputtering yields. For both CO/Ni and CO/Pd, the O$^+$ yields from Kr$^+$ bombardment increase with increasing beam velocity, similar to the behavior found for the oxidized targets. This is also true for Ar$^+$ bombardment of CO/Pd; however, the O$^+$ yields from Ar$^+$ bombardment of CO/Ni exhibit a plateau, or even a maximum, for the larger beam velocities. The O$^+$ yields from Ne$^+$ bombardment of CO/Ni increase slightly with beam velocity for the lower beam velocities, but
they decrease with increasing beam velocity for higher beam velocities. The O+ yields are essentially independent of beam velocity for Ne+ bombardment of CO/Pd. Thus, there are significant differences between the results for CO adsorption and those for O2 adsorption. Comparison of the secondary electron yields, as a function of beam velocity, from ion bombardment of O/Mo with those for CO/Ni (both shown in fig. 4.4) shows that the differences in the behavior of the O+ yields between O2 adsorption and CO adsorption cannot arise from any differences in the behavior of the secondary electron emission between the two adsorbates.

For CO/Ni, the O+ yields from Ar+ and Ne+ bombardment appear to lie on a common curve as functions of beam velocity, but the yields from Kr+ bombardment are twice as large. In a check for any influence of beam-induced electronic excitation, fig. 4.16a shows the O+ yields divided by Lindhard's electronic stopping power constant. The scaled yields for Ar+ and Kr+ bombardment fall on a common curve, while the scaled Ne+ yields are twice as large. If, as suggested in section 4.1.2, there exists a mechanism for O+ emission that is peculiar to Ne+ bombardment, it is conceivable that such a mechanism is operating for the CO/Ni system also. Nevertheless, there is no clear systematic behavior of the O+ yields as functions of beam velocity and beam species for ion bombardment of CO/Ni. Although the same mechanism for O+ desorption may be active for both O2- and CO-adsorbed targets for the lower beam velocities, the results for the higher beam velocities suggest the presence of either a different mechanism or an additional mechanism in the case of CO/Ni.
Comparison of the scale of fig. 4.15a with the scale of fig. 4.12a (considering the normalization of the O+ yields for the latter) reveals that the O+ yields from ion bombardment of CO/Ni are a factor of 4-10 greater than those from O/Ni. Madden, however, found the ESD yields of O+ from O/Ni to be much larger than those from CO/Ni [Ma76]. Both this discrepancy and the observation of the large enhancement of the Ni+ yield by CO adsorption suggest that the effects of CO adsorption on ionization probabilities merit further study.

The O+ yields from ion bombardment of CO/Pd (fig. 4.15b) do not fall on a common curve for the different beam species. Division by Lindhard's electronic stopping power constant (fig. 4.16b) improves the situation marginally, at best. The behavior of the O+ yields as a function of beam velocity for the Ne+ and Ar+ beams differs from that found for the CO/Ni targets. In fact, the behavior of the O+ yields from ion bombardment of CO/Pd resembles the proportionality to beam velocity found for the O2-adsorbate systems (excluding O/Ni), although the yields for Ne+ bombardment of CO/Pd exhibit less dependence on beam velocity than do those for Ne+ bombardment of the oxidized targets. Therefore, it appears that the desorption of O+ during ion bombardment of CO adsorbed onto metal surfaces is sensitive to the substrate metal.
Table 4.1
Ratios of measured secondary metal ion yields to calculated sputtering yields [Ma84] for 200 keV noble ion bombardment of adsorbate-covered transition metal surfaces. These ratios are the product of the transmission and angular acceptance of the quadrupole, the efficiency of the channeltron, and the ionization probability of the sputtered metal atom (none of which were measured separately).
<table>
<thead>
<tr>
<th>Target</th>
<th>Ne$^+$</th>
<th>Ar$^+$</th>
<th>Kr$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/Ti</td>
<td>$12 \times 10^{-6}$</td>
<td>$8.3 \times 10^{-6}$</td>
<td>$6.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>O/Nb</td>
<td>$2.3 \times 10^{-7}$</td>
<td>$1.5 \times 10^{-7}$</td>
<td>$1.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>O/Mo</td>
<td>$6.0 \times 10^{-7}$</td>
<td>$7.6 \times 10^{-7}$</td>
<td>$3.9 \times 10^{-7}$</td>
</tr>
<tr>
<td>O/W</td>
<td>$2.1 \times 10^{-8}$</td>
<td>$1.3 \times 10^{-8}$</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>O/Ni</td>
<td>-----</td>
<td>$5.6 \times 10^{-8}$</td>
<td>$4.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>CO/Ni</td>
<td>$6.4 \times 10^{-7}$</td>
<td>$9.0 \times 10^{-7}$</td>
<td>$8.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>CO/Pd</td>
<td>$4.1 \times 10^{-8}$</td>
<td>$2.8 \times 10^{-8}$</td>
<td>$2.8 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
Table 4.2
Slopes and y-intercepts computed by least-squares fits to the O\(^+\) yields and the secondary electron yields as linear functions of beam velocity, for 25-250 keV noble ion bombardment of oxidized transition metal surfaces. O\(^+\) yields are in units of \(10^{-7}\) per incident ion, electron yields are per incident ion, and velocity is in units of \(10^7\) cm/s.
<table>
<thead>
<tr>
<th>Target</th>
<th>Beam</th>
<th>Slope</th>
<th>Y-Intercept</th>
<th>Slope</th>
<th>Y-Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne⁺</td>
<td>Ar⁺</td>
<td>0.402</td>
<td>0.482</td>
<td>0.188</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.051</td>
<td>±0.493</td>
<td>±0.029</td>
<td>±0.024</td>
</tr>
<tr>
<td>Ti</td>
<td>Ar⁺</td>
<td>0.442</td>
<td>0.403</td>
<td>0.404</td>
<td>0.749</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.053</td>
<td>±0.269</td>
<td>±0.045</td>
<td>±0.179</td>
</tr>
<tr>
<td>Kr⁺</td>
<td>Ar⁺</td>
<td>0.461</td>
<td>0.026</td>
<td>0.612</td>
<td>-0.484</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.050</td>
<td>±0.186</td>
<td>±0.073</td>
<td>±0.338</td>
</tr>
<tr>
<td>Ne⁺</td>
<td>Ar⁺</td>
<td>0.153</td>
<td>2.05</td>
<td>0.269</td>
<td>0.763</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.026</td>
<td>±0.31</td>
<td>±0.023</td>
<td>±0.147</td>
</tr>
<tr>
<td>Nb</td>
<td>Ar⁺</td>
<td>0.406</td>
<td>-0.126</td>
<td>0.581</td>
<td>-0.350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.050</td>
<td>±0.221</td>
<td>±0.073</td>
<td>±0.314</td>
</tr>
<tr>
<td>Kr⁺</td>
<td>Ar⁺</td>
<td>0.414</td>
<td>0.277</td>
<td>0.683</td>
<td>-1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.029</td>
<td>±0.150</td>
<td>±0.040</td>
<td>±0.22</td>
</tr>
<tr>
<td>Ne⁺</td>
<td>Ar⁺</td>
<td>0.258</td>
<td>1.46</td>
<td>0.258</td>
<td>0.556</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.030</td>
<td>±0.30</td>
<td>±0.019</td>
<td>±0.122</td>
</tr>
<tr>
<td>Mo</td>
<td>Ar⁺</td>
<td>0.458</td>
<td>-0.258</td>
<td>0.438</td>
<td>-0.190</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.032</td>
<td>±0.120</td>
<td>±0.029</td>
<td>±0.108</td>
</tr>
<tr>
<td>Kr⁺</td>
<td>Ar⁺</td>
<td>0.624</td>
<td>0.062</td>
<td>0.590</td>
<td>-0.989</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.042</td>
<td>±0.186</td>
<td>±0.036</td>
<td>±0.165</td>
</tr>
<tr>
<td>Ne⁺</td>
<td>Ar⁺</td>
<td>0.0491</td>
<td>0.388</td>
<td>0.216</td>
<td>0.635</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.004</td>
<td>±0.049</td>
<td>±0.010</td>
<td>±0.090</td>
</tr>
<tr>
<td>W</td>
<td>Ar⁺</td>
<td>0.184</td>
<td>-0.243</td>
<td>0.424</td>
<td>-0.524</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.011</td>
<td>±0.056</td>
<td>±0.020</td>
<td>±0.088</td>
</tr>
<tr>
<td>Kr⁺</td>
<td>Ar⁺</td>
<td>0.275</td>
<td>0.004</td>
<td>0.467</td>
<td>-1.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.034</td>
<td>±0.152</td>
<td>±0.047</td>
<td>±0.20</td>
</tr>
</tbody>
</table>
Table 4.3

Ratios of the computed slopes for the O⁺ yields to the slopes for the secondary electron yields (table 4.2) and to the beam-dependent factor in Lindhard's electronic stopping power. Units for the first column are 10⁻⁷ O⁺ per secondary electron; units for the second column are arbitrary.
<table>
<thead>
<tr>
<th>Target</th>
<th>Beam</th>
<th>O$^+$ slope electron slope</th>
<th>O$^+$ slope Lindhard factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne$^+$</td>
<td>Ar$^+$</td>
<td>2.14</td>
<td>±0.43</td>
</tr>
<tr>
<td>Ti</td>
<td>Ar$^+$</td>
<td>1.09</td>
<td>±0.18</td>
</tr>
<tr>
<td></td>
<td>Kr$^+$</td>
<td>0.753</td>
<td>±0.121</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td></td>
<td>0.569</td>
<td>±0.108</td>
</tr>
<tr>
<td>Nb</td>
<td>Ar$^+$</td>
<td>0.699</td>
<td>±0.123</td>
</tr>
<tr>
<td></td>
<td>Kr$^+$</td>
<td>0.606</td>
<td>±0.055</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td></td>
<td>1.00</td>
<td>±0.14</td>
</tr>
<tr>
<td>Mo</td>
<td>Ar$^+$</td>
<td>1.05</td>
<td>±0.10</td>
</tr>
<tr>
<td></td>
<td>Kr$^+$</td>
<td>1.06</td>
<td>±0.10</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td></td>
<td>0.227</td>
<td>±0.022</td>
</tr>
<tr>
<td>W</td>
<td>Ar$^+$</td>
<td>0.434</td>
<td>±0.033</td>
</tr>
<tr>
<td></td>
<td>Kr$^+$</td>
<td>0.589</td>
<td>±0.094</td>
</tr>
</tbody>
</table>
Figure 4.1

Measured yields of Mo$^+$ (open circles), and Mo sputtering yields (closed circles) calculated as in [Ma84] and normalized to the measured Mo$^+$ yields at 200 keV (see table 4.1 for normalization factors), for bombardment of O/Mo by 25-250 keV noble gas ions:

a) Ne$^+$ bombardment; b) Ar$^+$ bombardment; c) Kr$^+$ bombardment.
Figure 4.2

$O^+$ yields per incident ion from 25-250 keV $Ne^+$, $Ar^+$, and $Kr^+$ bombardment of: a) $O/Ti$; b) $O/Nb$. 
(a) O/Ti

O$^+$ Yield (10$^{-7}$ / ion)

Beam Velocity (10$^7$ cm/s)

(b) O/Nb

O$^+$ Yield (10$^{-7}$ / ion)

Beam Velocity (10$^7$ cm/s)
Figure 4.3

O+ yields per incident ion from 25-250 keV Ne+, Ar+, and Kr+ bombardment of: a) O/Mo; b) O/W.
Figure 4.4
Secondary electron yields measured for 25-250 keV Ne⁺, Ar⁺, and Kr bombardment of: a) O/Mo; b) CO/Ni.
Beam Velocity (10^7 cm/s) vs. Electron Yield (/ ion)

(a) O/Mo

(b) CO/Ni
Figure 4.5
Yields of O\(^+\) from ion bombardment of O/Nb, divided by the beam-dependent factor in Lindhard's electronic stopping power to remove any dependence on electronic excitation.
Figure 4.6

Yields of $O^+$, divided by the beam-dependent factor in Lindhard's electronic stopping power to remove any dependence on electronic excitation, from ion bombardment of: a) O/Mo; b) O/W.
Figure 4.7

Periodic table of the elements, showing the transition metals and summarizing the behavior of \( \text{I}(\text{O}^+) \) as a function of beam velocity \( v \) (\( \propto v \): strict proportionality to velocity; \( \propto S_e \): proportionality to electronic stopping power; cascade: proportionality to sputtering yield from collision cascade).
<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
</tbody>
</table>

$\alpha_V \quad \alpha_V \quad \alpha_S \quad \alpha_S$
Figure 4.8

Secondary electron energy distribution measured for bombardment of O/V by 200 keV Ar+. The dashed line shows the background of "true" secondary electrons under the Auger feature as extrapolated from the distribution on either side of the Auger feature.
Figure 4.9

Behavior of the ESD cross-section for desorption of O\(^+\) from O/W as a function of incident electron energy. The solid line is the O\(^+\) yield, while the dashed line (solid dots) is the total O yield (from [Fe78]).
O\(^+\) FROM O\(_2\) - W

Desorption Cross Section

Electron Energy (eV)
Figure 4.10

Location of the maximum (upper panel) and half-width (lower panel) of the energy distribution of O\(^+\) desorbed from O/W by electron bombardment (from [We81]).
The diagram shows the variation of O^+ EDC peak energy and O^+ EDC half-width with electron energy for different surfaces, specifically O/W (110) and O/W (110). The peaks decrease as the electron energy increases, indicating a decrease in peak energy and increase in half-width with increasing energy.
Figure 4.11

Secondary electron energy distributions for bombardment of Mo by Ar⁺. Triangles: 2 keV; crosses: 5 keV; full circles: 10 keV; open circles: 15 keV (from [Be82]).
Figure 4.12

Yields of Ni⁺ and O⁺ (normalized to the Ni⁺ yield at 200 keV) from bombardment of O/Ni by 25-250 keV noble gas ions: a) Ar⁺ bombardment (O⁺ yields multiplied by 32.5); b) Kr⁺ bombardment (O⁺ yields multiplied by 15.1).
Figure 4.13

Secondary ion yields from bombardment by 25-250 keV Ar+: a) Ni$^+$ and CO$^+$ from CO/Ni (CO$^+$ yields multiplied by 324); b) Pd$^+$ and CO$^+$ from CO/Pd (CO$^+$ yields multiplied by 12.8).
(a) Ni$^+$ and CO$^+$ (scaled) as a function of beam velocity.

(b) Pd$^+$ and CO$^+$ (scaled) as a function of beam velocity.
Figure 4.14

Yields of Ni+ from 25-250 keV Ar+ bombardment of O/Ni and CO/Ni (yields from O/Ni multiplied by 12.5).
Figure 4.15

Yields of O+ from 25-250 keV Ne+, Ar+ , and Kr+ bombardment of:

a) CO/Ni; b) CO/Pd.
Figure (a) shows the yield of O\(^+\) ions as a function of beam velocity for CO/Ni. Different symbols represent different ions: Ne\(^+\), Ar\(^+\), and Kr\(^+\). Figure (b) presents the same data for CO/Pd.
Figure 4.16

Yields of O⁺, divided by the beam-dependent factor in Lindhard's electronic stopping power, for 25-250 keV Ne⁺, Ar⁺, and Kr⁺ bombardment of: a) CO/Ni; b) CO/Pd.
5.1. Summary

The emission of O\(^+\) secondary ions during ion bombardment of adsorbate-covered metal surfaces does not result from collision cascades, except for the target O/Ni. The other adsorbate/substrate systems studied can be divided into three categories. For the group consisting of O/V, O/Ti, and O/Nb, the yields of O\(^+\) increase linearly with incident ion velocity, which suggests that electronic processes are active. However, the expected scaling of the yields for different beam species on the basis of the electronic stopping power and the secondary electron yields is absent. The second group consists of O/Mo and O/W. For these targets, the emission of O\(^+\) can be more directly related to electronic processes; the scaling of the yields for different beam species resembles that of the electronic stopping power and the secondary electron yield. The emission of O\(^+\) from targets in these two groups behaves the same for metals in the same column of the periodic table. For these targets, however, the magnitude of the O\(^+\) yields is larger by a factor of about 2500 than that expected for desorption stimulated by secondary electrons. Nevertheless, since the yields of O\(^+\) from O/Ni result only from collision cascades, the behavior of the yields does appear to depend on whether the system can be maximally valent, as expected from the theory of ESD. This would make it difficult to propose a mechanism that does not invoke some form of electronic excitation.
For O/Nb, O/Mo, and O/W targets, the emission of O\(^+\) during Ne\(^+\) bombardment appears to have a component in addition to the velocity-proportional component. The mechanism for this additional emission is not known, nor is it understood why such a mechanism would not also operate for O/V and O/Ti.

The third group of systems studied consists of CO/Ni and CO/Pd. For these targets, the O\(^+\) yields are proportional to beam velocity for some beam species, but not for all; in the case of CO/Ni, the data exhibit a maximum rather than increase monotonically with beam velocity. No evidence was found for ion-induced electronically-stimulated desorption of CO\(^+\).

5.2. Further Experiments

There are further experiments that should be performed to enhance our understanding of ion-induced O\(^+\) emission. The metal oxide systems clearly require further study to determine which properties of the metal or metal oxide affect the details of the dependence of the O\(^+\) emission on beam velocity and beam species. In particular, other (potentially) maximally valent metal oxides located near Ti in the periodic table (such as Zr, Ta, and Re) should be examined to verify the apparent correlation of the behavior of the O\(^+\) emission with the column in the periodic table. Moreover, the electronic structure of the oxidized metal surfaces should be studied to determine whether maximally valent oxides are actually formed, as well as whether the behavior of the O\(^+\) emission correlates with any other variation in the electronic properties of the systems.
Systems known to be nonmaximally valent should also be further studied. The decrease in ion-induced ESD of O\(^+\) from other oxidized metals between V and Ni could be measured to determine whether the yields decrease gradually as one moves to the right in the periodic table or decrease suddenly when one begins to use nonmaximally valent oxides. The ion-induced emission of F\(^+\) and Cl\(^+\) from fluorinated and chlorinated transition-metal surfaces should also be studied, since these systems generally are not maximally valent.

Thus far, the only evidence that electronic processes are responsible for the ion-induced emission of O\(^+\) is that the O\(^+\) yields increase linearly with beam velocity, along with the scaling of the yields with electronic excitation in some cases. Measurements of the energy distribution of the O\(^+\) could provide further evidence, as the discussion in section 1.3 of the emission of F\(^+\) from fluorinated silicon shows. The signature of desorption induced by electronic processes would be a narrow energy distribution with a maximum at low energy, while a distribution with a maximum at high energy would implicate processes involving back-scattered primary ions. Since the offset of the O\(^+\) yields during Ne\(^+\) bombardment of some of the targets could be related to back-scattered Ne\(^+\), the energy distributions of O\(^+\) desorbed during Ne\(^+\) bombardment could help to explain these offsets.

There are other interesting primary beams that could be used. Bombardment by Ne\(^+\) beams with lower energy than used in this study should be examined. If the emission of O\(^+\) were to continue to decrease linearly with decreasing beam velocity, with an extrapolated nonzero yield at zero beam velocity, this would suggest that the additional emission of O\(^+\) is caused by some mechanism that is related
to the potential energy of the incident Ne+. If, however, the O⁺ yield were to become a nonlinear function of beam velocity and go to zero at zero beam velocity, then a mechanism invoking backscattered Ne⁺ could be implicated. Also, bombardment by lighter ions, such as He⁺, could yield interesting information on this phenomenon.

Study of the ESD of O⁺ from the oxidized metal surfaces used in this study would be useful for two reasons. First, such studies would allow the measurement of the ESD cross-sections as functions of electron energy for the specific systems studied under ion bombardment. This would allow a more accurate calculation of the integral of the product of the secondary electron distribution and the ESD cross-sections for these systems. Second, using the same mass spectrometer for both ion- and electron-beam studies would allow one to determine the absolute ratios of the ion-induced yields to the ESD yields, which would eliminate the problems associated with the lack of information about the transmission of the mass spectrometer when calculating the expected yield induced by secondary electrons.

Other possible experiments should concentrate on the emission of secondary electrons. Measurements of the electron energy distribution, and any Auger electron emission, are needed for targets other than O/V. In fact, it might be possible to measure coincidences between the emission of O⁺ and the emission of Auger electrons, if indeed the emission of O⁺ is related to an Auger-induced process. Such coincidence measurements could be particularly useful for determining the mechanism behind the offset of the O⁺ yields during Ne⁺ bombardment, particularly if Auger neutralization of the incident Ne⁺ is involved.
The CO-adsorbate systems also require further study by experiments using other ion beams and other metal substrates to better map out the behavior of the O+ emission. The use of targets of CO adsorbed onto such metals as Ti (at low temperatures, to avoid dissociation) would allow separation of the adsorbate-induced effects from the substrate-induced effects. Again, the emission of secondary electrons should also be examined, and experiments using primary electron beams should be performed, in order to determine whether the magnitude of the O+ yields is consistent with desorption induced by secondary electrons.
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