The role of adsorbed oxygen in secondary emission from metallic substrates

Scott Gregory Walton

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THE ROLE OF ADSORBED OXYGEN IN SECONDARY EMISSION FROM METALLIC SUBSTRATES

A Dissertation
Presented to
The Faculty of the Department of Physics
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

by
Scott Gregory Walton
August, 1998
APPROVAL SHEET

This dissertation is submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

Scott Gregory Walton

Approved, August 1998

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William E. Cooke

Dennis M. Manos

Kenneth G. Petzinger

Yicheng Wang

National Institute of Standards and Technology
For my parents,
Tom and Linda Walton

In loving memory of,
Anna E. Walton
"Nana"
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ABSTRACT

Low energy, ion- and photon-induced secondary electron and anion emission from metallic substrates has been investigated as a function of adsorbate coverage. Sodium positive ions (Na\(^{+}\)), with kinetic energies up to 500 eV, and photons, with energies up to 23 eV, are utilized to initiate secondary emission. The principal adsorbate is oxygen with coverages ranging from none to a few monolayers.

For ion-induced emission, the secondary electron and negative ion absolute and relative yields from 302 stainless steel and polycrystalline tungsten (W) have been measured as a function of both impact energy and oxygen coverage. Additionally, the yields from a "technical" stainless steel surface, i.e., a surface for which no in-situ cleaning is performed, have been measured. The sputtered anions have been identified by secondary ion mass spectroscopy (SIMS). For both surfaces, adsorbate coverage is found to greatly enhance the electron and anion yields at all impact energies.

In addition, the kinetic energies of the secondary electrons and negative ions have been measured as a function of both impact energy and oxygen coverage. The electron and anion kinetic energy distributions exhibit low most probable energies (1-2 eV) and unique features that are substrate dependent.

Photoelectron kinetic energy distributions for aluminum (Al), molybdenum (Mo), Mo (100) and stainless steel have been measured, as a function of oxygen coverage, in order to ascertain the effects of adsorbed oxygen. Additionally, photon-stimulated anion desorption from oxygen covered Al has been measured as a function of photon energy. This anion desorption is found to have a narrow resonance at approximately 8.75 eV.

The resonance in the photon-induced anion emission is shown to be in direct support of a model proposed to explain the observed ion-induced secondary electron and O\(^{-}\) emission from an oxygen covered Al surface. The model invokes a collision-induced excitation, of a surface state, that serves as a precursor to both electron and anion emission. This model is discussed in detail and utilized to explain the emission from oxygen covered stainless steel and tungsten. The results for the technical stainless steel surface are related to those for the oxygen covered surface and the implications for plasma discharge modeling are discussed.
THE ROLE OF ADSORBED OXYGEN IN SECONDARY EMISSION FROM METALLIC SUBSTRATES
CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

The interaction of energetic ions with metal surfaces has long been of interest for both its intrinsic value and because of the broad applications in many areas of physics. Indeed, as early as the middle of the last century the effects of interactions of ions with metal surfaces were first observed in gas discharges [1]. Early experiments designed to understand and quantify these interactions, namely, secondary ion emission resulting from ion impact were performed by Thomson [2], and Stark and Wendt [3]. Some years later, ion-induced electron emission from metal surfaces was observed by Penning [4]. The achievement of ultrahigh vacuum (UHV) and the appropriate surface diagnostic procedures in the middle of this century, partly driven by the needs of the semiconductor revolution, allowed for the preparation of atomically clean surfaces [5]. This also identified for the first time the effect of adsorbates on secondary emission. Since then, much effort has been focused on understanding the dynamics of ion-induced emission from adsorbate covered surfaces.

Photon-induced emission from surfaces has been observed for nearly as long as ion-induced emission from surfaces. In the late 1880's, Hertz [6] observed an increase in emission during electric discharge experiments when one of the electrodes is exposed to
ultraviolet radiation. Soon thereafter, Lenard [7] showed that ultraviolet light causes the emission of electrons from metal cathodes. This phenomenon, called the photoelectric effect, was later quantified by Milliken [8]. It was the observations of Hertz and Lenard that helped Einstein develop his quantum theory of the photoelectric effect [9]. In the 1950's it was realized that photon-surface interactions, in the form of X-ray photoelectron spectroscopy (XPS), could be used to characterize surfaces [10,11]. An important change in the study of photon-surface interactions was the discovery of synchrotron radiation in the late 1940's [12]. However, it wasn't until the late 1960's that serious effort was put into the design of electron accelerators dedicated solely to synchrotron research. These accelerators could provide intense, wide-band, tunable light sources; a requirement for the careful study of photoemission. One of the first electron accelerators, Tantalus, was the predecessor of Aladdin, the electron accelerator at the Synchrotron Radiation Center [13] where some of the experiments reported in this dissertation were performed. The creation of high power, tunable light sources allowed for a much better understanding of photoelectron emission and allowed for the first observations of photon-stimulated ion desorption [14]. Since those early machines, much of the work in photon spectroscopy has been dedicated to the study of adsorbate covered surfaces [15].

While it is clear that adsorbates play a crucial role in ion- and photon-induced emission, the dynamics of such emissions are not well understood [16,17]. An area of ongoing interest is the role of adsorbates in low energy, ion-induced secondary electron and anion emission, most notably, secondary electron emission. Conventional theories have been successful in describing the electron emission caused by ions with high impact energies (> 1 keV) but have only limited success in explaining the observations at lower impact energies.
energies. Similarly, much research has been devoted to photon-induced ion emission from adsorbate covered surfaces. Photon-stimulated desorption (PSD) typically utilizes photon energies on the order of several hundred eV, although, ion emission has been reported for photon energies as low as a few eV [18,19]. These efforts have focused primarily on positive and neutral, atomic and molecular emission with many investigations involving adsorbed layers on multi-component substrates and semiconductors [20,21]. The goal of this dissertation is to provide some insight concerning the dynamics of low energy, ion- and photon-induced secondary electron and anion emission from oxygen covered metallic substrates. In particular, the aim is to quantify and describe the role of oxygen in the observed secondary emission for ions with energies less than 500 eV and photons with less than 25 eV.

1.2 ION IMPACT

In the case of ion-induced electron emission, there are two mechanisms that are conventionally used to describe the process, the so-called potential and kinetic emission. The theory of potential emission, first described by Hagstrum in the mid 1950's [22], is characterized by a charge exchange between the incoming projectile and the surface. In Auger neutralization (AN), depicted in Fig. 1.1, an electron tunnels from the metal to an unoccupied energy level of the incoming ion, thus, neutralizing the ion. The energy released during this tunneling may be transferred to a second electron within the metal. If the energy transferred is sufficient to allow this second electron to overcome the surface work function, it may be emitted as a secondary electron. Then the requirement for secondary electron emission is that the energy level to which the electron tunnels, i.e., the
Fig. 1.1 The Auger neutralization process. The metal electron tunnels to the incoming ion ground state, which is the ionization potential (I.P.). A second electron within the metal gains the energy released in the tunneling and may leave the metal provided the I.P. is at least twice the work function (\(\phi\)).

ionization potential, must be greater than or equal to twice the work function.

If the incoming ion is in an excited, metastable state leaving a vacancy in the ground state, the vacancy could be filled by a process known as Auger de-excitation (see Fig. 1.2). For this process, the electron from the excited level is emitted if the unoccupied ground state is filled by an electron from the metal. If, however, the vacancy is filled by the electron from the excited level, the energy released during this de-excitation could be of sufficient energy to allow a surface electron to overcome the work function. The Auger de-excitation process is possible for ionization potentials greater than the work function but secondary electron emission requires that the difference between the excited level and the ground state is greater than the work function. Excitation of an incident ion to a metastable state can be achieved via collisions with the surface. This process, known as kinetic Auger excitation [13,23], involves the collisional excitation of the incident ion
Fig. 1.2 The Auger de-excitation mechanism. In this process, an electron in an excited state ($E_{ea}$) is either ejected (solid line) or de-excites to the ground state (dashed line) while the electron in the metal undergoes the other transition.

which may then decay by the Auger de-excitation.

In collisions with the surface, the incoming ion could transfer enough momentum to an electron in the metal causing it to be emitted. This so-called kinetic emission, requires that the energy transferred from the ion to the electron be sufficient to overcome the work function. Since the ratio of the ion mass to that of the electron is large, kinetic emission is only significant for impact energies where the ion velocity matches that of the electron at the Fermi level, viz., for ion energies of approximately 1 keV. Clear distinctions between potential and kinetic emission have been observed [24,25]. In fact, for low energy collisions (<1 keV), it is reasonable to assume that potential emission should be the dominant secondary electron emission mechanism, provided the ionization potential of the incoming ion is greater than or equal to twice the work function.

The emission of ions and atoms as a result of ion impact has been well studied [26-28] and is commonly referred to as sputtering. The two broad categories of sputtering are
chemical and physical sputtering. Chemical sputtering results from the collision-induced production of unstable compounds on the surface. The volatility of these compounds results in their desorption from the surface. Physical sputtering, like electron kinetic emission, involves a transfer of energy to the surface. If this energy is greater than the surface binding energy, atoms and/or ions may be emitted. In the case of low energy ions, the so-called single-knockon and collision-cascade regimes have had success describing the observed emission resulting from ion impact [29].

In the single-knockon regime the impacting ion transfers energy to a surface atom which may undergo a small number of collisions before being ejected. As the term implies, a transfer of energy from the primary ion to the target atom is responsible for the emission of that atom. The collision-cascade regime invokes a larger number of secondary collisions that occur within a given volume. These secondary and higher order collisions generate atoms that are energetic enough to cause a surface atom or atoms to be ejected. In this case, it is the secondary atoms that are responsible for emission of atoms. This model of emission, referred to as the Thompson-Sigmund model, has been successful in describing emission from clean as well as adsorbate covered surfaces [30].

Another result of kinetic energy transfer involves a collision-induced electronic excitation of surface species [31]. Generally characterized, the surface species are electronically excited by either direct ion, secondary atom, or secondary electron impact. This excitation can result in the emission of ions, excited species and/or atoms into the vacuum.

While the sputtering of neutrals is not a topic within this work, it is important to note that a neutral emitted from the surface may, via resonant charge transfer, be emitted as a
positive or negative ion. A theory describing this process invokes an electron tunneling model [32,33] and has been successfully used to describe some features of ion emission [34,35]. In this theory, the surface is described by a free electron “jellium” model [36] that is characterized by the work function and the emitted atom is characterized by its electron affinity and ionization potential. The electron affinity is used to describe negative ion emission while the ionization potential is used to describe positive ion emission. For negative ionization then, the electron affinity increases, approximately as an image potential, as the ion approaches the surface. For small distances (a few \(a_0\)), where the electron affinity exceeds the work function, an electron may tunnel to the atom thus creating a negative ion. In the case of dissociative chemisorption of oxygen for example, it is highly probable that oxygen resides on the surface as negative ion for low coverages.

### 1.3 PHOTON INTERACTIONS

The interaction of photons with surfaces produces secondary emissions similar to that of ion-induced emission with the difference being, of course, that there is not a fractional transfer of energy. This allows for the observation of resonant processes and reduces the interactions to local-site sensitivity with little effect on the neighboring bulk [17]. Photons with energies in the ultraviolet (UV) region are ideally suited to study surfaces where, for example, the penetration depth of 25 eV photons is typically no more than about 100 Å. Photoelectrons are emitted from either the valence band of the metal or from a bound atomic level. In a solid, the electrons near the Fermi level are the valence band electrons and are easily liberated when UV photons strike a surface [37].
Photoemission has been successfully described with a three-step model [38] involving the optical transition, transport to the surface, and escape to the vacuum. In the case of bound state electrons, an optical transition results in the release of the electron from its bound state. The subsequent migration of the electron to the surface can reduce its energy by collisions with atoms or other electrons. The final escape to the vacuum results in a further loss of energy in overcoming the surface work function. The latter two steps are readily observed in the photoelectron kinetic energy distribution, commonly referred to as an energy distribution curve (EDC). UV spectroscopy is a powerful tool in determining the surface characteristics of clean and adsorbate covered surfaces via their electron states.

Photon-induced ion or atom emission from metals can be categorized as either photodesorption or photon-stimulated desorption (PSD). The former refers desorption from photon-induced molecular or crystalline vibrations and phonons. PSD, on the other hand, refers to photon-induced electronic excitations that led to desorption. The mechanisms for photon-stimulated ion desorption (PSID) follow those proposed for electron-stimulated ion desorption (ESID). One such mechanism, the Knotek-Feilbelman mechanism [39], requires the photoemission of a core electron with the vacancy being filled by an electron from a second atom. The vacancy in the second atom may, in turn, may be filled by electron from another atom. If the electron lost in any atom is not replaced (now making it an ion) and it is near the surface, it could be emitted from the surface by coulombic expulsion. Another mechanism, described by Menzel and Gomer [40] and Redhead [41] (the so-called MGR theory) invokes a Franck-Condon [42] transition to an antibonding molecular state which will dissociate, leading to desorption. While core excitations can require photons in the x-ray domain, excitations in the MGR
theory only require UV range photons.

1.4 SECONDARY EMISSION: A COMMON MECHANISM?

For experimental reasons, the mechanisms for secondary emission have typically been studied separately. Because of this, theories describing the two processes have also been developed separately but there are some clear parallels between them. This is particularly true in the case of ion emission. Knotek, Jones, and Rehn [14], in their efforts to explain the first observation of photon-stimulated desorption (PSD), directly invoke the Knotek-Feilbelman mechanism proposed to explain electron-stimulated desorption (ESD). In summary they state, “The thresholds for PSD and ESD are in remarkable agreement and leave little doubt that the two proceed by the same mechanism.” Both photon- and electron-stimulated emission processes are considered within the realm of desorption induced by electronic transitions (DIET) [43-47]. The physics of DIET can be describe as a localized electronic excitation that leads to desorption where the electronic energy is converted to nuclear kinetic energy [47]. This should not be surprising since the momentum transfer in photon-atom and electron-atom collisions should not be sufficient to explain emission.

In a similar fashion, low energy, ion-induced secondary electron emission is explained by the theory of potential emission where Auger neutralization is the driving mechanism. As described earlier, it has been demonstrated that collisions can induce excited surface states that may provide a precursor to electron and ion emission. It is not unreasonable, therefore, to assume the secondary emission produced by low energy ion, electron, and photon interactions with surfaces share a common mechanism.
1.5 SECONDARY EMISSION: APPLICATIONS

The interactions of energetic ions with surfaces have broad applications. Of fundamental importance to any surface experiment is *in situ* cleaning by ion bombardment, commonly called sputter-cleaning. It typically utilizes noble gas ions with kinetic energies on the order of 1-5 keV to remove surface contaminants. In the case of low energy ions, an understanding of ion-surface interactions is critical for industries that utilize gas discharges in plasma processing. In fact, secondary electron emission from cathodes is required for the maintenance of the plasma in a DC discharge. In the sheath region between the plasma and the cathode, the number of positive ions exceeds the number of electrons and, as a result, the potential in this region is typically on the order of a few hundred volts. This causes the ions to be accelerated toward the cathode while the electrons and negative ions are extracted into the plasma. The conditions in this region (including the ratio of electrons to ions and the associated kinetic energies) are vital to an understanding of the dynamics of a discharge plasma and will be largely determined by the interactions at the surface.

In order to produce the plasma, certain conditions must be met. For example, in the Townsend discharge, where space-charge effects can be neglected, the criterion for initiating the discharge can be written as $\gamma ( e^{\alpha d} - 1 ) = 1$, where $\gamma$ is the coefficient of secondary electron emission induced by positive ions colliding with the cathode, $d$ is the separation of the cathode and anode, and $\alpha$ is a constant [48]. Although $d$ and $\alpha$ are significant, it is quite clear that the "ignition" of the discharge can not be achieved if the secondary electron emission coefficient is zero. While secondary electron emission is fundamental, the secondary ion emission is just as important in terms of the ion density.
within the sheath. The emission of negative ions from the cathode would result in a decrease of the positive potential and hence less ions would strike the cathode. This, in turn, would decrease the secondary electron emission and so forth until the discharge could be extinguished, a condition known as “flame-out”. The role of adsorbates in this process will alter the emission from the cathode in a similar way. Since it has been shown that adsorbed oxygen significantly enhances secondary electron emission [49,50], the removal of oxygen from the cathode by ion-induced sputtering would reduced the electron emission such that the discharge could, in principle, be extinguished.

1.6 EXPERIMENTS

The aim of this dissertation is to investigate secondary electron and negative ion emission from metallic substrates initiated by low energy ions and photons with particular attention to the effect of adsorbed oxygen. For the ion impact experiments, sodium positive ions, with energies ranging from 50 eV to 500 eV, are chosen to initiate the secondary emission. Sodium is chosen to eliminate the potential emission of electrons, since the ionization potential (~ 5.1 eV) is much less than twice the work function of most metals. It is also the case that for these impact energies, the kinetic emission of electrons is improbable. The ion impact experiments were performed at the College of William and Mary and the photoemission experiments were performed at the Synchrotron Radiation Center utilizing photons with energies up to 23 eV. The effect of oxygen on secondary emission is limited to low coverages since it is not the intention to study the effect of oxide overlayers formed on metals. Therefore, in all experiments oxygen exposures were such that the coverage ranged from none to a few monolayers.
The primary metals chosen in these experiments are: stainless steel, tungsten, molybdenum, and aluminum. Stainless steel is chosen because of its wide use in many areas of physics. Stainless steel is almost exclusively used in the fabrication of ultrahigh vacuum systems and components; in plasma and discharge physics, the electrodes used are often made of stainless steel. An understanding of the interactions of energetic ions with the oxygen covered stainless steel is important since most functional surfaces have some form of oxygen coverage.

Tungsten (W) is commonly used as a filament since its high melting point is ideally suited for thermionic electron emission. Tungsten also has the benefit of being one of the most studied metals. Both the secondary emission and oxygen adsorption properties are well documented.

Molybdenum (Mo) and aluminum (Al) are included in the photoelectron experiments since their ion-induced secondary emission properties were previously studied in this laboratory [49,51,52]. Aluminum, in particular, is chosen to study photon-stimulated ion desorption and the results will be related to its ion-induced secondary emission properties, which have recently been described with a model [51]. The use of different metals allows for a comparison of secondary emission properties and, hence, the role of adsorbed oxygen in different substrate-adsorbate systems.

Historically, the principal observable in secondary emission investigations has been the yield. The yield, otherwise known as the secondary emission coefficient, is defined as the number of emitted products per incident particle. For the present ion impact studies, the secondary electron and negative ion yields have determined as a function of both the impact energy and oxygen coverage. The kinetic energy distributions of the secondary
products have also been measured and Secondary Ion Mass Spectroscopy (SIMS) has been used to identify the secondary anions. Photoelectron spectroscopy of the surfaces has been utilized to examine the effects of adsorbed oxygen. In addition, experiments involving photon-stimulated anion desorption are compared with the predictions of an electronic excitation mechanism previously developed to explain low energy, ion-induced emission from oxygen covered aluminum [51] and molybdenum surfaces [52]. In what follows, this excitation mechanism is first reviewed because it is central to the subsequent discussions. This is followed by a discussion of the experimental apparatus and methods. Finally, the results of the experiments on the aforementioned substrates will be presented and discussed. A portion of the information contained in this dissertation may be found in:


CHAPTER 2

A MECHANISM FOR THE EMISSION OF ANIONS AND ELECTRONS

For low-energy ion-surface interactions, the presence of adsorbates has been shown to greatly affect secondary electron emission [49-54]. While it is not always the case, the secondary electron yield generally increases when small quantities of adsorbates (on the order of a monolayer) are present on the surface [16]. In the case of oxygen adsorption, it has been known for sometime that the increase in the secondary electron yield can be an order of magnitude or more [16]. Curiously, the reasons for this enhancement were not well understood. Recent experimental work in this laboratory resulted in the development of a model designed to explain the measured secondary electron and anion emission from oxygen covered aluminum [51]. This model invokes a mechanism that provides for and reproduces many of the observations for secondary electron and anion emission. A review of the model is necessary as it will prove useful in explaining the observed emission from other oxygen covered substrates caused by both ion and photon impact.

2.1 OBSERVATIONS FOR ALUMINUM

The effect of oxygen coverage is demonstrated in Fig. 2.1 where the secondary electron and negative ion yields, resulting from the impact of Na⁺, are shown as a function of impact energy for varying exposures. Throughout this work, the exposure is expressed...
Fig. 2.1 (a) The absolute electron yields, as a function of impact energy, for Na$^+$ impacting Al. Shown are the yields for a clean (■) surface and surfaces exposed to 50 L (○) and 100 L (▲) of oxygen. (b) The absolute O$^-$ yields as a function of impact energy for the same surface conditions.

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Fig. 2.2 (a) The absolute $O^-$ (●) and electron (▲) yields, as a function of oxygen exposure, for 150 eV Na$^+$ impacting an Al surface. (b) The absolute yields for 350 eV Na$^+$ impacting an Al surface.

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Fig. 2.3 (a) The electron to anion ratio, as a function of oxygen exposure, for 150 eV Na⁺ impacting an Al surface. (b) The ratio for 350 eV Na⁺ impacting an Al surface.
in terms of the Langmuir (L), where one L is defined as $10^{-6}$ Torr-s. In other words, exposing a surface to a gas at a partial pressure of $10^{-6}$ Torr for one second is equivalent to an exposure of one L. If all gas molecules that come in contact with the surface "stick", an exposure of one L would result in complete coverage, or one monolayer of adsorbed gas. It is generally agreed that oxygen is dissociatively adsorbed on aluminum with a sticking coefficient of ~ 1% and, hence, an exposure of 100 L corresponds to a surface coverage, $\Theta_s$, of ~ 1.0 monolayer of oxygen atoms [55-57].

SIMS analysis shows O' is, by far, the dominant secondary anion (94%) with trace amounts of AlO' (5%) and AlO$_2$' (<1%). Therefore, the secondary anion yield is essentially the O' yield. Fig. 2.1 shows the presence of oxygen on the surface greatly increases both the secondary electron and O' emission compared with those observed for a clean surface. While the greatest effect is for higher energies, it appears that a common threshold exists for O' and electron emission for impact energies around 50 eV. Fig. 2.2 illustrates the dependence of the yield on oxygen coverage for impact energies of 150 eV and 350 eV. The increase in emission is most dramatic for exposures up to 100 L ($\Theta_s = 1$ monolayer) with a smaller increase in emission from 100 L to 300 L. The electron to O' ratio is given in Fig. 2.3 and, like the yields, is observed to increase for exposures up to ~ 1 monolayer where the ratio reaches a maximum and remains constant.

Kinetic energy distributions for the secondary products are given in Fig. 2.4. The electron distributions have a Gaussian shape with a peak at ~ 1.0 eV and widths of 1.0 - 1.5 eV that broaden slightly with increasing impact energy. The O' distributions exhibit a similar peak around 1.0 eV but the distributions are asymmetric with a low-level tail at higher kinetic energies. As should be expected from the yield measurements, the
Fig. 2.4 (a) The electron kinetic energy distributions resulting from 350 eV (▲) and 150 eV (Δ) Na⁺ impacting an Al surface exposed to 100 L of oxygen. (b) The O⁺ kinetic energy distributions resulting from 350 eV (●) and 150 eV (○) Na⁺ impacting the surface for the same conditions.
distributions differ with respect to the intensity, but otherwise are more-or-less independent of impact energy and coverage. It should be emphasized that there exists no further structure in the kinetic energy spectra for energies greater than those shown.

The salient features of ion-induced secondary emission can be summarized as follows: (1) Oxygen coverage greatly increases secondary electron emission. (2) There exists a common threshold for O' and electron emission for impact energies in the vicinity of 50 eV. (3) Both the O' and electron kinetic energy distributions share a similar most probable energy and (4) the distributions are, to a large degree independent of coverage and impact energy.

2.2 ELECTRON EMISSION

As discussed earlier, the use of Na⁺ as the incident ion precludes potential emission which requires the incoming ion to have an ionization potential of at least twice the work function. For Na⁺, with an ionization potential of 5.1 eV, impacting Al, with a work function 4.2 eV, this is not the case. If however, the work function of Al was greatly decreased by the presence of oxygen it might be possible for potential emission to be the source of secondary electron emission. Photoemission measurements have shown, however, that the work function decreases only slightly as oxygen accumulates on the surface (refer to chapter 4 of this work). This and other measurements [51,54] have concluded that the increased emission cannot be attributed solely to an oxygen-altered work function. Another possible source of secondary electrons could be via auto-ionizing O** or auto-detaching levels of (O')* if those species are sputtered from the surface [53]. The electrons resulting from such mechanisms would exhibit kinetic energy spectra with

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discrete features in the range of 8 eV to 20 eV [58,59]. This, however, is not observed in
the electron kinetic energy distributions which exhibit no structure above a few eV.

One of the interesting features of the secondary emission is the apparent correlation of
O' and electron emission. The emissions are correlated in the sense that the secondary
yields appear to share a common threshold and increase in a similar manner with oxygen
coverage. An exothermic charge transfer collision between the incoming Na+ and an O
residing on the surface could result in the simultaneous emission of an electron and
O' [49]. If this occurs, an autocorrelation spectrum should be easily identified due to the
difference in flight times of the electrons and O' from the surface to the detector.

Autocorrelation studies found no evidence for such correlated emission [51]. Artificially
generated data sets adjusted to mimic experimental observations suggested that a
correlation as small as 0.1% would have been observed. Hence, one can conclude that the
simultaneous emission of O' and an electron does not occur. With the inability of these
mechanisms to provide for the observed electron emission, another mechanism must be
identified.

2.3 O' EMISSION

The adsorption of oxygen can be described in terms of dissociative chemisorption.
Calculations by Bahrim et al. [60] of the energy and width of the affinity level of O' as a
function of distance from an Al surface show that for small distances, the magnitude of the
affinity level, $E_a(z)$, exceeds the surface work function. If this is the case, it is
energetically favorable for the vacancy on the oxygen atom to be filled by an electron from
Fig. 2.5 The electron affinity level, $E_A(z)$, of O$^-$ as a function of distance from an Al surface. The shift of $E_A(z)$ is essentially that predicted by an image potential. Also shown is the width, $\Delta(z)$, of the affinity level and the distance, $z_a$, where the affinity level is equal to the work function, $\phi$. For $z < z_a$, it is favorable for the existence of O$^-$.

The dynamics of sputtering mechanisms describing the removal of substrate atoms have been well established [26-28]. The collision-cascade mechanism, in particular, has been used to describe the sputtering for energies above a few hundred eV [61] and to describe the removal of adsorbates from the surface [30] and can be used in an attempt to characterize the emission of O$^-$ from the surface. Let us assume that O$^-$ is, somehow, ejected from the surface as a result of Na$^+$ impact. For an oxygen anion outside the aluminum surface, the probability that it survives as a negative ion is related to the electron decay width for a given atomic level and is expressed as

$$P = \exp \left[ - \int_{i_o}^{z(t)} \Delta[z(t)] \, dt \right], \tag{2.1}$$

where $\Delta[z(t)]$ is the decay width for the atomic level.
Using Eq. (2.1), the probability that $O^-$ survives its journey to the vacuum can be written as

$$P_{\text{ion}}^\infty [v_z(z)] = \exp \left[ - \int_{z_a}^{\infty} \frac{\Delta_m(z) \, dz}{v_z(z)} \right], \quad (2.2)$$

where $\Delta_m(z)$ is the resonance width, $v_z(z)$ is the ion's exit velocity normal to the surface, and $z_a$ is the distance from the surface where $|E_A(z_a)| = \phi$ [62]. The exit velocity of the ion as it leaves the surface is determined by considering force due to a simple image potential, $q/4z$. In atomic units then,

$$v_z(z) = \sqrt{\frac{2}{M} \left[ E + \frac{1}{4} \left( \frac{1}{z} - \frac{1}{z_a} \right) \right] \cos \theta}, \quad (2.3)$$

where $M$ is the mass of $O^-$ and $E$ is the initial kinetic energy as it begins its journey to the vacuum. Eq. (2.2) then becomes

$$P_{\text{ion}}^\infty [E, \theta] = \exp \left[ - \int_{z_a}^{\infty} \frac{\Delta_m(z) \, dz}{\sqrt{\frac{2}{M} \left[ E + \frac{1}{4} \left( \frac{1}{z} - \frac{1}{z_a} \right) \right] \cos \theta}} \right], \quad (2.4)$$

The widths for the Al/O system have been approximated by

$$\Delta_m(z) = \Delta_{mo} e^{-\gamma_m z^2}, \quad (2.5)$$

where $\Delta_{mo}$ is the resonance width of a given magnetic substate and $\gamma_m$ is a constant. The widths have been calculated by Bahrim et al. [60] for the Al/O system and their calculated values will be used. The collision-cascade theory predicts the initial energy, $E$, to have a
distribution of the form \([29,63]\)

\[
E_{\text{ion}}^{\infty}(E, \theta) = \left[ \frac{C E}{(E - U)^2} \right] \cos(\theta) , \tag{2.6}
\]

where \(C\) is constant and \(U\) is the surface binding energy with a value on the order of a few eV. The energy distribution for \(O^+\) that survives into the vacuum for a given magnetic substrate, averaged over all angles (assuming azimuthal symmetry), is then given by

\[
S_{\text{ion}, m_i}^{\infty}(E) = \frac{1}{2\pi} \int E_{\text{ion}}^{\infty}(E, \theta) P_{\text{ion}, m_i}(E, \theta) \, d\Omega . \tag{2.7}
\]

The \(O^+\) kinetic energy distribution for all three magnetic substates is obtained by summing over the substate distributions:

\[
S_{\text{tot}}^{\infty}(E) = \frac{1}{3} \sum_{m_i = 0, \pm 1} S_{\text{ion}, m_i}^{\infty}(E) . \tag{2.8}
\]

The resulting distribution can be directly compared to the measured kinetic energy distributions as seen in Fig. 2.6. The failure of the Eq. (2.8) to fully account for the experimental results is clearly seen; It cannot provide for the low energy peak found in the observed distribution. The maximum of the collision-cascade distribution [Eq. (2.6)], which occurs at \(E=U/2\), is moved to much higher energies by the ion survival probability term [Eq. (2.4)], which is a sharply increasing function of \(E\). This suppresses the low energy ions, meaning that the low energy ions lose the electron and become neutrals.

There are no physically plausible adjustments that will bring the predictions of Eq. (2.8) into agreement with the observed distributions. While the predictions of the collision-cascade mechanism may agree with the \(O^+\) distribution at higher kinetic energies (i.e., the
Fig. 2.6 The observed (●) O⁻ kinetic energy distribution for 450 eV Na⁺ impacting an Al surface exposed to 100 L of oxygen and the dashed line is the calculated distribution of the collision-cascade mechanism from Eq. (2.8).
“tail” in the distribution), it is clear that a mechanism is needed to provide for the low energy peak around 1.0 eV.

2.4 O\textsuperscript{-} AND ELECTRON EMISSION: A MECHANISM

As noted there has been no proposed mechanism that will adequately model the observed O\textsuperscript{-} kinetic energy spectra nor is there one that will account for the electron emission in any respect. A recently proposed mechanism [51,52] that can provide for both O\textsuperscript{-} and electron emission, is depicted schematically in Fig. 2.7. This proposed mechanism requires a collisionally-induced excitation that serves as precursor to both O\textsuperscript{-} and electron emission. The surface state, AlO\textsuperscript{-}, is collisionally excited by the impacting Na\textsuperscript{+} to an antibonding state, (AlO\textsuperscript{-})\textsuperscript{*}, via a Frank-Condon (vertical) type excitation. The (AlO\textsuperscript{-})\textsuperscript{*} can then decay by O\textsuperscript{-} emission and survive to the vacuum or the O\textsuperscript{-} may decay by electron emission. The electron may be ejected into the vacuum or back to the metal. The schematic diagram of this process (Fig. 2.7) is clearly an oversimplification. But like the MGR model of electron-stimulated desorption [40,41], it serves as a guide to understanding the excitation mechanism.

Let us assume the probability for excitation, $P_x(z)$, is represented by a Gaussian distribution centered at the equilibrium position, $z_{eq} = 3.25 \, a_0$, of the adsorbed O\textsuperscript{-} with respect to the reflection plane,

$$ P_x(z) = \sqrt{\frac{b}{\pi}} \exp\left[ -b \left( z - z_{eq}\right)^2 \right], \quad (2.9) $$

where $b^{1/2}$ is the width of the distribution. After excitation, the ion may exit the surface and survive as a negative ion or it may decay by electron emission. Decay by electron
Fig. 2.7 Schematic diagram of the molecular states for the interactions of oxygen and $O^-$ with an Al surface as a function of distance from the surface. The AlO and AlO$^-$ ground states are isolated molecular curves that represent many possible surface states. Also shown are the electron decay widths used to describe the decay to the metal, $\Delta_m(z)$, and to the vacuum, $\Delta_v(z)$.

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emission is characterized by either decay to the metal or decay to the vacuum, the latter of which will result in a secondary electron. Decay by electron emission to the vacuum is limited by the crossing point, \( z_c \approx 4.5 \, a_o \), of the \((\text{AlO'})^*\) and the AlO curves while decay to the metal can occur for any distance. This is represented by the decay widths shown below the potential energy curves in Fig. 2.7 where \( \Delta_M (z) \) and \( \Delta_V (z) \) correlate to the decay to the metal and to the vacuum respectively.

Like the collision-cascade mechanism, the kinetic energy distributions via this excitation mechanism may be calculated. The probability that \( \text{O}^- \) survives to the vacuum can be written as

\[
P_{\text{ion}}^{\text{ex}} (z) = \exp \left[ - \int_{z}^{\infty} \frac{\Delta_{\text{Tot}}(z)}{v(z)} \, dz \right],
\]  

(2.10)

where \( \Delta_{\text{Tot}}(z) \) is the total decay width and \( v(z) \) is the exit velocity determined by the \((\text{AlO'})^*\) potential. The total decay width is given by

\[
\Delta_{\text{Tot}}(z) = \Delta_M(z) + \Delta_V(z),
\]  

(2.11)

where again, the decay widths are approximated by

\[
\Delta_V(z) = \Delta_{V_e} \exp(- \gamma_V \, z)
\]  

(2.12)

and

\[
\Delta_M(z) = \Delta_{M_e} \exp(- \gamma_M \, z).
\]  

(2.13)
The exit velocity is given by,

$$v(z) = \sqrt{\frac{2}{M} K_{\text{ion}}^{\text{ex}}(Z)} ,$$

(2.14)

where $K_{\text{ion}}^{\text{ex}}(z)$ is the kinetic energy of $O^-$ as it leaves the surface along the $(AlO^-)^*$ curve. The kinetic energy is a function of the energy associated with its position along the $(AlO^-)^*$ curve and any initial momentum transfer in the collision. The energy above the vacuum level for the $(AlO^-)^*$, at a given distance, may be approximated by

$$\delta E_{\text{ion}}^{\text{ex}}(Z) = E_s \left(\frac{z_{eq}}{z}\right)^2,$$

(2.15)

where $E_s$ is the energy of the $(AlO^-)^*$ curve at the equilibrium distance, $z_{eq}$. Then the kinetic energy of the ion as it exits the surface at a distance, $z$, after excitation at a distance, $z_i$ (where $z > z_i$), is given as

$$K_{\text{ion}}^{\text{ex}}(z) = \delta E_{\text{ion}}^{\text{ex}}(z_i) \left[ 1 - \left(\frac{z}{z_i}\right)^2 \right] + K_i ,$$

(2.16)

where $K_i$ is the initial kinetic energy of the ion resulting from the momentum transfer in the collision. The kinetic energy distribution for the $O^-$ ions which survive to the vacuum is then given by

$$S_{\text{ion}}^{\text{ex}}(E) = \frac{1}{E_n^2} P_x(z) P_{\text{ion}}^{\text{ex}}(z) \delta E_{\text{ion}}^{\text{ex}}(z) ,$$

(2.17)

where $E_n$ is a normalization constant determined by the total integrated survival probabilities. The meaning of this distribution can be described as follows: If the excitation via ion impact occurs [with a probability, $P_x(z)$], and an emitted $O^-$ survives to the vacuum [with a probability, $P_{\text{ion}}^{\text{ex}}(z)$], then its kinetic energy will be $\delta E_{\text{ion}}^{\text{ex}}(z)$. Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The electron kinetic energy distribution can be calculated in a similar fashion. The probability of electron emission is related to O\textsuperscript{−} emission and is given as

\[
P_{\text{electron}}^{\text{ex}}(z) = \left[ 1 - P_{\text{ion}}^{\text{ex}}(z) \right] \left[ \frac{\Delta_{\nu}(z)}{\Delta_{\text{tot}}(z)} \right],
\]

where the first term is the probability that O\textsuperscript{−} does not survive to the vacuum and the second term is the fractional electron decay to the vacuum. The kinetic energy associated with the electron emission to the vacuum is the difference between the \((\text{AlO})^{*}\) and the AlO curves. The electron kinetic energy is estimated by assuming linear potentials with a crossing point, \(z_c\), given by

\[
\delta E_{\text{electron}}^{\text{ex}}(z) = F_c(z_c - z).
\]

As for O\textsuperscript{−} [Eq. (2.16)], the kinetic energy of the electrons is then given as

\[
S_{\text{electron}}^{\text{ex}}(E) = \frac{1}{E_n^2} P_{\text{ex}}(z) P_{\text{electron}}^{\text{ex}}(z) \delta E_{\text{electron}}^{\text{ex}}(z).
\]

The resulting distributions, based on the potentials of Fig. 2.7, are given in Fig. 2.8 along with the experimental results. In the case of O\textsuperscript{−} emission, the result from Eq. (2.17) is summed with the result from the collision-cascade mechanism [Eq. (2.8)] to provide a reasonable fit. In this way, the collision-cascade mechanism supplies the high energy tail and the excitation mechanism supplies the low energy peak. The resulting electron distribution is also in good agreement with the experimental results. The values of the parameters used in the calculations are given in Table 2.1.

Before concluding this discussion, it should be noted that it is possible to calculate the relative yields for the ions and electrons from the survival probabilities of Eqs. (2.17)
Fig. 2.8 (a) The experimental (O) O\textsuperscript{−} kinetic energy distribution for 450 eV Na\textsuperscript{+} impacting an Al surface exposed to 100 L of oxygen. Also shown are the calculated distribution of the collision-cascade mechanism (—), as predicted by Eq. (2.8), and the distribution of the excitation mechanism (—), as predicted by Eq. (2.17). The sum of these distributions represents the total distribution (—). (b) The experimental (Δ) electron kinetic energy distribution for the same impact energy and surface conditions and the excitation mechanism distribution (—), as predicted by Eq. (2.20).
Table 2.1 The parameters used in fitting the theoretically predicted electron and O' kinetic energy distributions to the observed distributions.

**Excitation Mechanism Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>1.4 eV</td>
</tr>
<tr>
<td>$K_t$</td>
<td>0.1 eV</td>
</tr>
<tr>
<td>$E_n$</td>
<td>0.46 eV $a_o^{-1/2}$</td>
</tr>
<tr>
<td>$b$</td>
<td>0.3 $a_o^{-2}$</td>
</tr>
<tr>
<td>$F_c$</td>
<td>0.6 eV $a_o^{-1}$</td>
</tr>
<tr>
<td>$z_{eq}$</td>
<td>3.17 $a_o$</td>
</tr>
<tr>
<td>$z_c$</td>
<td>4.35 $a_o$</td>
</tr>
<tr>
<td>$\Delta V_0$</td>
<td>0.0215 eV</td>
</tr>
<tr>
<td>$\gamma V$</td>
<td>0.119 $a_o^{-1}$</td>
</tr>
<tr>
<td>$\Delta M_0$</td>
<td>1.0 eV</td>
</tr>
<tr>
<td>$\gamma M$</td>
<td>0.9 $a_o^{-1}$</td>
</tr>
</tbody>
</table>

**Collision-cascade Mechanism Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_a$</td>
<td>3.17 $a_o$</td>
</tr>
<tr>
<td>$C$</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>$U$</td>
<td>1.0 eV</td>
</tr>
<tr>
<td>$\Delta M_0$ $m_l = 0$</td>
<td>2.414 eV</td>
</tr>
<tr>
<td>$\gamma M_0$ $m_l = 0$</td>
<td>0.731 $a_o^{-1}$</td>
</tr>
<tr>
<td>$\Delta m_0$ $m_l = \pm 1$</td>
<td>3.172 eV</td>
</tr>
<tr>
<td>$\gamma M_0$ $m_l = \pm 1$</td>
<td>0.630 $a_o^{-1}$</td>
</tr>
</tbody>
</table>
and (2.20). This, of course, assumes that the probability for excitation is unity and is accomplished by integrating over all energies:

$$Y_{\text{ion}, e}^{\text{ex}} = \int_0^\infty S_{\text{ion}, e}(E) \, dE. \quad (2.21)$$

These calculations are instructive and will be discussed later.

To summarize, in an effort to explain the observed emission from an oxygen covered Al surface, a collisional excitation of a surface state was proposed. This excited state serves as a precursor to both $O^-$ and electron emission. In addition to providing a mechanism for the observed electron emission, the model can, with reasonable parameters, produce results in good agreement with the observed electron kinetic energy distributions. In the case of $O^-$ emission, the excitation mechanism, in conjunction with the collision-cascade, mechanism provides an ion kinetic energy distribution that is also in good agreement with experimental observations. The molecular potential energy curves of Fig. 2.7 are intended to serve as a guide to understanding the excitation mechanism.

A goal of this work will be to further understand this mechanism and to test its viability in explaining the results for the low energy, ion-induced secondary emission from other substrates. Perhaps, in a more important test of the model, photon-induced anion emission will be investigated to see if the excitation of the $\text{AlO}^-$ state depicted in Fig. 2.7 can also be achieved with photons. As can be inferred from Fig. 2.7, photons with energies between about 8 and 10 eV would be required for such an excitation.
Chapter 3

Experimental Methods

The apparatus described herein was designed for the specific purpose of studying low energy, ion- and photon-induced emission from metal surfaces. The investigations of ion-induced secondary electron and negative ion emission were performed at The College of William and Mary while the investigations of photon-induced electron and negative ion emission were performed at The Synchrotron Radiation Center [13]. For ion-induced emission, the primary observable is the absolute yield. The apparatus was configured to collect all secondary negative products, identify them, and determine the associated kinetic energy spectra. The photoemission studies were performed utilizing synchrotron radiation which provides an intense, tunable, low energy photon source. In these experiments, the primary observable is the photoelectron kinetic energy distribution. However, the photoemission apparatus could be configured to determine the relative photon-induced yields for electrons and negative ions separately. In order to understand the effects of oxygen on ion- and photon-induced secondary emission, it is necessary to produce well-characterized surfaces, a requirement satisfied by ultrahigh vacuum (UHV) conditions and in vacuo cleaning and diagnostic capabilities. Both systems will be described, in detail, in this chapter.
3.1 ION-INDUCED SECONDARY EMISSION EXPERIMENTS

3.1.1 Vacuum system

The experimental apparatus shown schematically in Fig. 3.1 is composed of two subsystems: a UHV chamber in which all of the experiments were conducted and an adjoining gas handling system. The UHV chamber, capable of achieving base pressures less than $2 \times 10^{-10}$ Torr, is a Varian (model FC-12E) table top vacuum chamber. It is stainless steel and all flanges are copper sealed, including the top which is sealed by a 12" Wheeler flange. The chamber vacuum is maintained by a 260 l/s turbomolecular-drag pump, five 50 l/s sputter ion pumps, and a titanium sublimation pump. The turbomolecular-drag pump is connected to the chamber via a 6" port that can be isolated by a pneumatic gate valve, while the ion pumps and the sublimation pumps are contained within the chamber. All turbomolecular drag pumps mentioned are backed by rotary vane pumps. The total pressure in the chamber is monitored by a Bayard-Alpert ion gauge and an Ametek Inc. residual gas analyzer (model MA100MF) is used to monitor both the total pressure and the partial pressure of a given species.

Two differentially pumped chambers are attached to the main chamber. The differential line containing the argon ion gun is maintained by another 260 l/s turbomolecular-drag pump. The pump can be isolated from the argon ion gun by a pneumatic valve (2.75") and the pressure is monitored by a Bayard-Alpert ion gauge. When not operating, the pressure in this differential line is less than $8 \times 10^{-10}$ Torr. The housing containing the electrostatic energy analyzer (EEA) is pumped by a 100 l/s sputter ion pump. The pressure, monitored by the ion pump controller, is less than the controller can read, viz., $10^{-8}$ Torr, and is assumed to be an order of magnitude less.
Fig. 3.1 A schematic of the ion-induced secondary emission experimental apparatus. The gas handling system is shown at the bottom of the schematic and the UHV chamber at the top. The ion pumps attached to the UHV chamber are shaded and all valves are represented by (⊗). The flanges without labels are for electrical feedthroughs. Not shown in the schematic are the rotary vane pumps that back the turbomolecular-drag pumps (Turbo pumps).
The gas handling system contains two reservoirs and is connected to the main chamber by three variable, precision leak valves capable of $10^{-11}$ Torr·l/s leak rates. The reservoirs contain high purity argon and oxygen but are capable of holding other gases. The vacuum in the gas handling system, maintained by a 60 l/s turbomolecular drag pump, is less than $10^{-9}$ Torr when fully evacuated and is monitored by a Bayard-Alpert ion gauge. The gas reservoirs are separated from the turbomolecular pump by manual metal-seal valves. The leak valve on the oxygen line is connected to the main chamber and is responsible for oxygen exposure during the experiments. An additional line, directly to the turbomolecular-drag pump, is available to evacuate the line between the oxygen reservoir and the leak valve connected to the main chamber. In this way, the line to the chamber may be evacuated while the oxygen reservoir remains pressurized. The argon line is connected to the argon ion gun by two leak valves making it possible to introduce argon gas to the ionization cell and charge transfer cell independently, allowing for the production of both positive ion and neutral argon beams.

3.1.2 Experimental arrangement

The experimental configuration, located in the center of the UHV chamber, is shown in Fig. 3.2. It was designed to optimize the collection efficiency of the secondary products while at the same time allowing for the ion beams (Na⁺ and Ar⁺) to impact only the surface being studied. A sodium positive ion gun is aligned at 60° with respect to the surface normal. The ion gun consists of an ion source, an einzel lens, and a quadrupole lens all of which are contained within a grounded shield. A final focusing lens is attached to and isolated from the end of this shield. The ion source, manufactured by Spectra-Mat Inc., is
Fig. 3.2 A schematic diagram of the experimental apparatus within the UHV chamber. Depicted are the ion and electron guns along with the extraction lens stack. The surface normal is represented by the dotted line that extends from the surface and is coaxial with the symmetry axis of the extraction lens stack. The split lens is contained within lens three.
highly porous tungsten into which sodium has been fused. When heated, the source will emit Na\(^+\) with an emission purity that is reported to be better than 99% [64] and when operating, the source does not increase the pressure in the chamber. For most experiments, the Na\(^+\) current on the surface is 1-3 nA for kinetic energies between 30 and 500 eV.

Opposite the sodium ion gun and also aligned at 60° with respect to the surface normal is an argon gun manufactured by Fisons (model EX05F). It has the capability of producing both positive ions (Ar\(^+\)) and neutral atoms (Ar\(^0\)) in the range of 0.1-5.0 keV and its primary function is for sputter cleaning. In the ion mode, argon gas is admitted to the ionization cell; in the neutral mode, argon is admitted to both the ionization and charge transfer cells simultaneously. Typically, the Ar\(^+\) current measured on the surface is 1.5 \(\mu\)A at an energy of 4.0 keV. When used for sputter cleaning the argon beam can be rastered across the entire surface area. The rastering is controlled by a VG Electrovac Ltd. imaging unit (model 346) that can be used, in conjunction with a Stanford Research Systems amplifier (model SR570) connected to the sample, to produce an image of the surface. This is accomplished by connecting the rastering and surface signals to an oscilloscope. Setting the oscilloscope in the x-y mode produces a elementary image of the sample by monitoring the surface current intensity (z-input) as a function of the Ar\(^+\) beam position. While this image is not capable of great detail, it does serve to ascertain that the Ar\(^+\) beam is rastered over the entire surface.

An electron gun, aligned at 30° with respect to the surface normal, is used for Auger electron spectroscopy (AES). At 3 keV, it is capable of producing an electron beam at the surface of approximately 15 \(\mu\)A. Typical commercial AES systems are designed such that
the electron beam is incident along the surface normal with the secondary electrons also collected along the surface normal which allows for detailed, quantitative surface analysis. For this system, such a design is not possible. However, since the Auger measurements are used to provide only a confirmation of adsorbed species, the configuration is sufficient.

Secondary electrons and negative ions emitted from the surface are collected along the surface normal. The surface is mounted vertically on a holder in a plane perpendicular to the plane of the sodium, argon and electron guns. This holder is electrically isolated so that the surface can be biased while the ion and electron currents are measured; biasing is essential for complete collection of secondary products. Isolation also allows for resistive heating by passing current through the samples. Located behind the surface is a planar, transparent tungsten grid that is also biased to assist in focusing the products toward the extraction lenses. In order to further focus the products and impose a degree of cylindrical symmetry in the extraction optics, a cylindrical grid is placed around the surface and extends from the surface to beyond the beginning of the extraction stack. Holes are cut in the cylindrical grid so that the sodium, argon, and electron beams may pass. An electrometer can be attached to both grids to assist in Na\(^+\) beam focusing and secondary emission collection.

The extraction lens stack, aligned along the surface normal, is an electrostatic lens system that serves as the primary collection and focusing device. Its twofold purpose is to measure the secondary yields and to deliver the secondary products to the electrostatic energy analyzer. The lens stack, shown in Fig. 3.2, is comprised of five lenses, one of which is a split lens. Lens one, located closest to the surface, is biased to collect a majority of the secondary products. Typically, it is found that lens one collects...
70-80% of the secondary products. Attached to lens two is a small electromagnet that is used to sweep the electrons from the total negatively charged products. A split lens is contained within and isolated from lens three. The two halves of the split lens are electrically isolated and can be biased to collect or pass the secondary products. In the collection mode, the split lens is used to determine the ratio of electrons to anions.

Lens four is the final focusing lens prior to entry into the EEA.

In order to ensure that all of the secondary electrons and anions emitted from the surface are collected and focused, the location and potential of each component of the experimental configuration, shown in Fig. 3.2, is critical. These conditions are determined, in part, using SIMION®, software developed by the Idaho National Engineering Laboratory. SIMION® simulates the trajectories of charged particles in the presence of electrodes which serves as a guide to optimizing the collection and focusing efficiency of the system. An example of such a simulation is shown in Fig. 3.3 for the potentials typically used in these experiments.

The EEA is a double focusing, electrostatic energy analyzer manufactured by Comstock Inc. (model AC-901B). It consists of two concentric spherical sector surfaces with an average radius of 36.5 mm [65]. A Galileo Corp. channel electron multiplier (CEM), located at the end of the surfaces, is used for particle detection. The EEA is capable of transmitting particles at various energies and, as with most energy analyzers, the lower the transmission energy, the better the resolution. The energy resolution is found by: first, measuring the kinetic energy of secondary electrons ejected by a 1.0 keV Ar⁺ beam at several transmission energies; then, determining the full width at half maximum (FWHM) of the kinetic energy spectrum for each transmission energy; and,
Fig. 3.3 SIMION® ion trajectory simulations for the experimental apparatus found in Fig. 3.2. The voltage for each element is (from bottom to top): Planar Grid, -19.7 V; Surface, -20.0 V; Cylindrical Grid, -43.8 V; Lens one, 70.0 V; Lens two, 272.2 V; Lens three 116.8 V; Split Lens (both halves), 90.0 V; Lens four, 45.4 V. For this simulation, the negative ions leave the surface with initial kinetic energies ranging from 0.5 to 5.0 eV. The anions are ejected from points that extend across the surface with angles up to 30° from the surface normal.

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finally, plotting the FWHM, $\Delta E$, as function of the transmission energy, $E_{\text{trans}}$. The slope, $\Delta E / E_{\text{trans}}$, is the resolution and is found to be 0.008. The primary function of the EEA is to measure kinetic energy distributions of the secondary electrons and anions. It is also used to perform Auger electron spectroscopy (AES) by determining the secondary electron energy spectra generated by the 3 keV electron beam. However, it may be operated in a fixed energy, low resolution mode that allows for time of flight (TOF) and, hence, secondary ion mass spectroscopy (SIMS) measurements.

The physical apparatus described above requires substantial control and measurement capabilities. The voltage control of the various elements is done with either direct connection to power supplies or indirect connection through an array of voltage dividers since control on the order of 0.1 V is typically required. Data gathering and device control, when possible, is automated by computer. Lab Windows® programs were written to allow a PC, equipped with a National Instruments GPIB 488-IEEE card, to interface with all control and measurement devices. This included data collection from the Keithley programmable electrometers (models 617 and 485), an Aston GPIB scalar (model 721), a Fluke digital multimeter (model 45), and the RGA. Those collection devices correspond to the yield, kinetic energy, TOF, and partial pressure measurements. The voltage of the elements of the EEA and the current to the electromagnet are set by Kepco programmable power supplies (model APH 500M), which are controlled by Kepco digital programers (SN 488-122).
3.1.3 Measurements

In order to measure the absolute secondary yields, the extraction stack is operated in a mode that allows for the measurement of the anion and electron yields. This is done by first measuring the total yield \( Y_{T^-} \) for all secondary products and then subtracting the ion yield \( Y_{X^-} \) from the total yield to determine the electron yield \( Y_{e^-} \). In practice this is accomplished by biasing the split lens to collect all secondary products reaching the split lens. Because of hysteresis in the electromagnet located at lens two, the current supplied to the electromagnet must be carefully set to maximize the collected secondary emission current prior to subsequent measurements. This maximized emission current ensures there is no magnetic field at lens two, viz., all of the electrons are collected. The absolute yield is then determined by

\[
Y_{T^-} = \frac{I^{-}_{\text{Lens 1}} + I^{-}_{\text{Split Lens}}}{I^{-}_{\text{Surface}} - (I^{-}_{\text{Lens 1}} + I^{-}_{\text{Split Lens}})},
\tag{3.1}
\]

where the signs of all the currents are taken to be positive. The ion yield is separately determined by supplying current to the electromagnet and measuring the split current. The current to the electromagnet creates a transverse magnetic field, on the order of 80 Gauss, severely defocusing the electrons so that they do not reach the split lens. It should be noted that while the field is strong enough to separate the electrons from the ions, it does not appreciably affect the ion trajectories. It is straightforward then to determine the anion and electron yields using

\[
Y_{X^-} = Y_{T^-} \left( \frac{I^{\text{Split Lens w/ B-field}}}{I^{\text{Split Lens w/o B-field}}} \right),
\tag{3.2}
\]
and

\[ Y_{e^{-}} = Y_{T^{-}} - Y_{X^{-}} , \]  

(3.3)

where it is assumed that the electron-ion ratio measured at the split lens is equivalent to the ratio for all or the secondary products. This assumption is supported by the observation that the ratio is constant for a wide range of extraction stack focal conditions.

The extraction stack focal conditions can be adjusted to pass all secondary products to the EEA by biasing the two halves of the split lens at the same potential. The kinetic energy distributions are measured at a fixed transmission energy and hence a fixed resolution. Typically, a transmission energy of 40.5 eV is chosen and, with a resolution of 0.008, the FWHM attributable to the analyzer is 0.32 eV. The kinetic energy distributions of the negative products are measured in a similar fashion to the yield measurements. That is to say, the electromagnet is used to separate the electrons from the anions and the spectra for each are measured. An additional feature of the kinetic energy distributions is that they may be used to verify that the surface is the source of secondary products; a shift in the surface voltage is directly correlated to a shift in the energy scale of the distributions.

As a diagnostic tool, the EEA can be used for AES studies. For AES, a transmission energy of 82.5 eV, corresponding to a spread of 0.66 eV, is found to be the most practical. The primary function of the AES studies is to determine if oxygen is present on the surface. For each experiment a surface cleaning procedure is established, in part, by observing a characteristic oxygen signal, in this case, the KLL transition. Since the energy difference between the K and L shells is approximately 503 eV, the characteristic Auger...
electrons will have this kinetic energy. The lack of such electrons then satisfies at least one criterion for surface cleanliness. A secondary function is to verify metal purity. It is not uncommon to observe a significant carbon signal or to observe small signals from trace impurities. Cleaning techniques, described later, are used to eliminate or substantially reduce these signals.

As mentioned earlier, TOF-SIMS measurements are also made using the EEA. In this case, the transmission energy is fixed at 40.5 eV and the kinetic energy is chosen in order to maximize the transmitted anion intensity. The measurements are made by chopping the Na⁺ beam and using a Stanford Research Systems multi-channel scalar (model SR430) to record the TOF spectrum. The Na⁺ beam is pulsed by a Direct Energy Inc. fast high voltage switch (model GRX-1.5-E). The switch, driven by an external pulser, ramps the voltage on the third lens of the Na⁺ ion gun between a high and a low voltage. The high voltage blocks the Na⁺ beam from hitting the surface (approximately 20 V above the source voltage) while the low voltage focuses the beam on the surface. Typically, the chopped Na⁺ is incident on the surface for 1.0 µs at a frequency of 5 kHz. Assuming the kinetic energy and distance traveled is the same for all products reaching the CEM, the products can be identified, via the masses, by

\[ \frac{M_1}{M_2} = \frac{t_{1}^{2}}{t_{2}^{2}}, \]  

(3.4)

where the values of \( t_{1,2} \) are given relative to the electron peak in the TOF spectrum, which is used to approximate the "zero" of the TOF-SIMS scale. The assumption of equivalent distances is subject to error since the trajectories of products leaving the surface at
different emission angles are clearly not the same. TOF-SIMS measurements are also used to verify surface cleanliness since the presence of a species other than that of the substrate would indicate surface contamination.

3.1.4 Surface preparation

The stainless steel and tungsten surfaces are 50 mm x 3 mm polycrystalline ribbons. The thickness for each is, respectively, 0.076 and 0.05 mm. The stainless steel sample is stainless steel 302 shim stock while the tungsten is laboratory grade and reported to be 99.9% pure [66]. Prior to placement into the vacuum, the surfaces are ultrasonically cleaned in a solution of Acetone followed by a solution of Methanol to remove any oils. After ultrasonic cleaning, the surfaces (as well as any other piece of equipment used in the vacuum) are handled with vinyl gloves since any grease would out-gas for a considerable amount of time and cannot be removed by in situ cleaning techniques. Once in the vacuum system, the surfaces are annealed in a high oxygen environment for about an hour to eliminate carbon contamination, which is confirmed by AES.

Before each experiment, the surface must be free of oxygen. In order to accomplish this, repeated cycles of Ar$^+$ sputtering and high temperature annealing are utilized. While cleaning times and sputter energies for each surface are different, the process involves: rastering the Ar$^+$ beam across the surface, followed by annealing, and then repeating the process. For resistive annealing, currents in excess of 5 A are passed through the ribbon causing it to glow orange in color. Similar resistive heating tests done at atmosphere showed the temperature corresponding to this orange, measured by a thermocouple, is in excess of 600° C. The Ar$^+$ energies and sputtering times to achieve cleanliness and are

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Table 3.1  
A comparison of parameters used in attaining clean surfaces.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ar⁺ energy (keV)</th>
<th>rastering time (min)</th>
<th>1st annealing time (min)</th>
<th>2nd annealing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>4.0</td>
<td>60</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3.5</td>
<td>45</td>
<td>5</td>
<td>.5</td>
</tr>
</tbody>
</table>

given in Table 3.1. The cleaning method for each sample is established by measuring the total yield for a Na⁺ impact energy of 250 eV. Yield measurements show that there is a minimum in the total negative product sputtering yield for which no increase in cleaning times could reduce. Once this value is determined, cleanliness is further verified by observing no detectable levels of surface contaminants by both AES and TOF-SIMS. These criteria then define a clean surface.

Oxygen exposure is achieved via a precision leak valve while the oxygen partial pressure is monitored by the residual gas analyzer (RGA). The dose is given in Langmuir \[ 1 \text{ Langmuir (L) = 1x10^{-6} Torr-s } \] and is determined by simply integrating the partial pressure as a function of time given by the RGA. The partial pressure during exposure can be determined with an accuracy of ± 15%. It should be noted that there is no direct means of determining surface coverage in this system and so the measured results are given in terms of oxygen exposure. Since it is known that the presence of alkali metal effects the secondary emission [53,67,68], great care is taken to keep the sodium dose to a minimum during the experiments. During the experiments the sodium dose is limited to 20 nA·min but is usually less. For sample sizes given above and an assumed sticking coefficient of 1.0 Na/Na⁺, this dose results in a coverage of $10^{-3}$ monolayers. The effects of sodium coverage can, however, be instructive and will be utilized in this work. As will
be shown, it takes a considerable dose to appreciably effect the yields, so there was no attempt to adjust the measured yields to account for the effect of accumulated sodium.

3.2 PHOTOIN-INDUCED SECONDARY EMISSION EXPERIMENTS

The experiments were performed at the Synchrotron Radiation Center (SRC) in Stoughton, Wisconsin [13]. The accelerator [69], with a circumference of 88.9 m, provides an 0.8 or 1 GeV electron beam with initial average currents of 225 mA and 150 mA, respectively. The current degrades in time so that electrons need to be injected into the accelerator every four to eight hours, depending on the beam energy. The photons arise from synchrotron radiation resulting at 12 separate bending magnets providing photon energies ranging from 1 eV to nearly 6 keV.

3.2.1 Experimental apparatus

The experiments were performed on the Stainless Steel SEYA beam line [69] which is connected to a UHV chamber in which the experiments are conducted and is shown schematically in Fig. 3.3. The beam line consists of 5 focusing mirrors and a monochromator. The monochromator is a Seya-Namioka [70-72] type with a gold coated spherical grating designed by American Holographic. The radius of curvature is 998.8 mm and consists of 1200 lines/mm with a useful wavelength range from 250Å (49.6 eV) to 2500Å (4.96 eV). Located before and after the monochromator are adjustable slits that range from 0.005 to 0.5 mm for the entrance slit and 0.04 to 0.5 mm for the exit slit. The FWHM of the photon energy is determined by the multiplying the entrance/exit slit width by the reciprocal linear dispersion of the monochromator.
Fig 3.4 A schematic diagram of the significant components of the photon-induced secondary emission experimental apparatus. The CMA and the surface are contained within the UHV chamber, which is connected to the beamline. The beamline extends from the accelerator to the UHV chamber and contains the other components shown. Also shown is the magnetic field utilized for the photon-stimulated desorption experiments.
(8.33 Å/mm) for slit widths greater than 0.1 mm. The photon flux also scales linearly for slit widths greater than 0.15 mm. Located after the final focusing mirror are three filters: two aluminum filters that pass photons with wavelengths between 175 Å (70.5 eV) and 800 Å (15.5 eV), where the extinction coefficient sharply increases for wavelengths above 800 Å [73]; and a LiF filter, for which the transmittance increases sharply for wavelengths above 1050 Å (11.8 eV) [74]. Diagnostic gold and GaAsP diodes, located after the final focusing mirror, are provided to determine the intensity of the photon beam. The gold diode is useful for energies above 10 eV and the GaAsP is suited for lower energies.

A 90% transmitting Ni mesh, located near the exit flange, is used to determine the in situ photon flux. The described optics are designed to produce an image at the surface with spot size of 2 mm x 1 mm.

The experiments are conducted in a bakeable UHV chamber connected to the exit flange of the beamline which has a base pressure after bakeout of ~ 2 x 10^{-10} Torr. The chamber was designed and built by the SRC to study photoelectron spectroscopy. The main diagnostic tool is an energy analyzer intended to measure photoelectron kinetic energy spectra. The analyzer, a double pass cylindrical mirror analyzer (CMA) designed by PHI Inc. (model 15-255G), collects a spatially integrated photoemission signal. The energy resolution of the CMA is determined by measuring the 10% - 90% edge width of Ir (111) cooled to 150° K and is found to be 160 meV and 225 meV at pass energies of 5 eV and 10 eV [69]. An electron gun, coaxial with the extraction optics of the CMA, allows for Auger electron spectroscopy (AES).

A differentially pumped sample introduction chamber attached to the main chamber includes a three-sample load lock and feedthrough for sample transfer into the main
chamber. Also attached to the chamber is a differentially pumped gas manifold that contains oxygen and argon. Precision leak valves allow for the introduction of those gases into the chamber. A sample holder, within the chamber, has three degrees of freedom that allows for easy sample manipulation. The holder is equipped with a filament for sample heating via electron bombardment and a thermocouple to monitor the sample temperature. An Ar⁺ ion gun, capable of providing a 10μA, 1 keV beam, is also provided. A Stanford Research Systems RGA (model RGA100), brought from William and Mary, is connected to one of the free ports of the UHV chamber to allow for precise partial pressure measurements.

The photon source and the CMA are located in a plane that is perpendicular to the plane of the surface and are separated by an angle of 90°. The surface is situated so that the surface normal is 45° with respect to both the incident photons and the center line of the energy analyzer. The surface is biased at -20 volts to assist in electron collection.

3.2.2 Measurements

The electron distributions are measured using beamline entrance and exit slit widths of 0.300 mm. For 10 eV photons the FWHM of the photon beam is 0.0202 eV and for 23 eV it is 0.1066 eV. Assuming the CMA and monochromator resolutions add in quadrature, the total resolution for the kinetic energy distributions is taken to be 0.16 eV for 10 eV photons and 0.19 eV for 23 eV photons. An energy distribution curve (EDC) is obtained by averaging repeated energy scans. A decrease in the photon flux resulting from a constantly degrading accelerator current needs to be accounted for when taking energy distributions and the photocurrent of the Ni mesh is used when comparing emission.
intensities of the EDC's so that each EDC can be normalized to the photocurrent. It should be noted that for an EDC, averaged over ten scans, the photocurrent decreases by less than 10%.

For the photon stimulated desorption (PSD) experiments, a “proof of principle” experiment was performed. The apparatus and procedures for data acquisition were altered to allow for the appropriate measurements. First, a large electromagnet is placed on the outside of the CMA housing to create a magnetic field perpendicular with the center line of the CMA where the field strength is sufficient to alter electron trajectories such that they cannot traverse the CMA. This field, however, is not strong enough to completely defocus the anions transmitted through the CMA. The field strength is unknown because the experimental setup did not allow for in situ measurements due to the μ-metal shielding inside the CMA housing. For anion detection, the mode of collection is altered such that the emission as a function of incident photon energy can be recorded. This is achieved by setting the CMA to rapidly scan a small range of kinetic energies near threshold. In practice, this results in an energy scan of 3.0 eV beginning slightly below the zero of the energy scale, which is determined by the surface potential. The pass energy of the CMA is set at 100 eV since this optimizes collection efficiency and resolution is largely irrelevant for these studies. The count rate is then recorded at separate photon energies ranging from 10.5 eV to 6.0 eV. The addition of a LiF filter near the exit aperture of the beam line, while slightly decreasing photon flux, ensures that no higher order photons from the monochromometer are incident on the surface.
3.2.3 Sample preparation

Sample preparation was similar to that for the ion-induced emission experiment since a comparison of both ion- and photon-induced emission is intended. Prior to each measurement, the samples are cleaned by alternating cycles of Ar$^-$ sputtering and high temperature annealing. The samples are sputter cleaned using a defocused 1 keV, 10 μA Ar$^+$ beam and the samples are annealed by electron bombardment. This cycle is then repeated with sputtering and annealing times comparable to those given in table 3.1. During electron bombardment, the surface electron current is on the order of 1 mA with a surface temperature > 700° C. The exception to this, aluminum, was heated indirectly to avoid sample destruction. Surface cleanliness is determined by AES such that no detectable levels of oxygen are observed. The only contaminant is carbon which is only observable in trace quantities. Oxygen exposure is accomplished by admitting O$_2$ into the chamber while observing its partial pressure with the RGA. As with the ion-induced experiments, the exposure, in terms of Langmuir, is calculated by integrating the pressure over time and is used in reporting the results since there is no way of directly determining surface coverage.
CHAPTER 4

PHOTON-INDUCED EMISSION

Ultraviolet photoelectron spectroscopy (UPS), which includes photon energies in the range of 10-150 eV, is a useful tool in the study of surfaces and adsorbate-surface interactions. Because the mean free path of UV photoelectrons is typically less than 10 Å for most materials [36,75], UPS is sensitive to the first few atomic layers of the surface. Additionally, the valence electron photo-cross section is large for UV photons [36]. Photon energies used in these investigations (< 25 eV) then serve as an ideal probe of the surface valence band which extends 5-10 eV from the Fermi level for most materials [37], where the Fermi level is determined by the work function. The electron energy distribution, or the density of states (DOS), within the valence band is not smooth and varies depending on the metal. The adsorption of oxygen, as would be expected, alters both the work function and the DOS. For a given metal, the photoelectron kinetic energy spectrum, commonly referred to as an energy distribution curve (EDC), is utilized to determine both the work function and the DOS.

Photon-stimulated ion desorption (PSID) invokes an electronic excitation that serves as a precursor to ion desorption. In a similar fashion, the model in chapter 2 describes a mechanism for secondary electron and anion emission resulting from low energy, ion impact. The model invokes a collision-induced electronic excitation to an antibonding
state which serves as the initial step in $O^-$ and electron emission from oxygen covered
metallic surfaces. If the model is realistic, photon-induced $O^-$ emission from oxygen
covered metallic surfaces should also be observable. The purpose of these experiments is
to determine the effects of adsorbed oxygen on the surface and to explore the possibility
of low energy, photon-stimulated ion desorption, a means of ascertaining the validity of
the model discussed in chapter 2. For this reason, aluminum was chosen to investigate
low energy, photon-stimulated desorption.

4.1 PHOTOELECTRON EMISSION

4.1.1 Emission spectra

The band structure in a solid is determined by the energy and momentum relationships
within a metal. Primary photoelectrons leaving a metal with a given energy and direction
contain information about the band structure of the metal. Angle resolved photoemission
measurements can be utilized to determine the band structure by measuring the emission at
a given angle and energy, i.e. the electron momentum and energy. On the other hand,
age integrated photoemission measurements, the type performed here, determine the
number of electrons at a given energy integrated over all momenta. The EDC for angle
integrated photoemission then reflects the electronic density of states, or in other words,
the number of electrons at a given energy. Fig. 4.1 illustrates how the relevant features
correspond to the EDC. Electrons leaving the surface with the largest kinetic energy are
those electrons coming from the Fermi level. Below the Fermi level, the electrons in the
valence band are described by the DOS and the electrons with near-zero kinetic energy
define the onset of electron emission. The kinetic energy of the photoelectrons is related
Fig. 4.1 An illustration of the relationship between the electron energies within a metallic solid and the photoelectron kinetic energy spectrum (from Ref. [75]).
to the electron binding energies within the metal using the Einstein equation,

\[ E_{KE} = h\nu - E_{BE} - \phi, \quad (4.1) \]

where \( E_{KE} \) is the electron kinetic energy, \( h\nu \) is the photon energy, \( E_{BE} \) is the electron binding energy relative to the Fermi level, and \( \phi \) is the work function of the metal.

Considering Eq. (4.1), the work function can be determined from the EDC. First, consider the difference between the onset and the Fermi level kinetic energies,

\[ E_{KE}(\text{Fermi}) - E_{KE}(\text{onset}) = (h\nu - E_{BE} - \phi)_{\text{Fermi}} - (h\nu - E_{BE} - \phi)_{\text{onset}}, \quad (4.2) \]

\[ E_{KE}(\text{Fermi}) - E_{KE}(\text{onset}) = -(E_{BE})_{\text{Fermi}} + (E_{BE})_{\text{onset}}. \quad (4.3) \]

Given the binding energy at the Fermi level is zero, the binding energy for the electrons at the onset are then

\[ \Delta E_{KE} = (E_{BE})_{\text{onset}}, \quad (4.4) \]

where \( \Delta E_{KE} \) is the width of the EDC. The surface work function is found by substituting Eq. (4.4) into Eq. (4.1) for the conditions, \( E_{KE} = 0 \), at the onset of photoemission,

\[ \phi = h\nu - \Delta E_{KE}. \quad (4.5) \]

While these features are readily observed in the EDC, the Fermi level and the onset are subject to inherent uncertainties. Thermal broadening results in an EDC that is broadened about the true Fermi energy. The onset, on the other hand, is affected by potential differences between the sample bias and the collection apparatus, the analyzer transmission
energy, and the analyzer work function [76,77]. Given these uncertainties, the absolute value of the surface work function is difficult to ascertain with great accuracy. But, since most of these variables are held constant during and between measurements, the change in the work function as a result of oxygen coverage can be determined with a much greater accuracy of, say, ~ 0.01 eV. The method to determine the work function and its change will be discussed later.

4.1.2 Clean surfaces

Shown in Fig. 4.2 are EDC’s for clean surfaces using an incident photon energy of 23 eV. The zero of the kinetic energy is determined, in part, by the surface potential. For these measurements, the surface is biased at approximately -20 V to assist in the collection efficiency. The onset of emission is observed when the CMA is set to measure electrons with a kinetic energy of 20 eV. Electrons ejected from the Fermi level appear with a kinetic energy in the vicinity of ~ \( h\nu + 20 - \phi = 38 \) eV. The structure in the EDC at higher energies is indicative of the electron DOS and clearly varies for each metal. Superimposed on the EDC is the emission due to electrons arising from secondary processes that is characterized by a peak at low kinetic energies followed by a decay from the peak to the Fermi edge. This feature of secondary emission is primarily the result of inelastic scattering during electron transport to the surface. It corresponds to those electrons which have lost energy prior to leaving the surface or to those electrons that have gained sufficient energy to leave the surface in the inelastic collisions. While the determination of the surface work function is fundamentally possible from the EDC, in practice this involves some inherent experimental uncertainties, as noted above. The electron
Fig. 4.2 Photoelectron spectra for clean, polycrystalline aluminum, molybdenum, and stainless steel (302). The incident photon energy is 23 eV and the surface is biased at -20 V to increase collection efficiency. The ordinate for Al is logarithmic while for Mo and stainless steel, the ordinates are linear.
distribution at the Fermi level is given by the Fermi distribution,

\[
    n(E) = \frac{1}{e^{\left(\frac{E - E_F}{kT}\right)} + 1},
\]

(4.6)

where \(E\) is the electron energy, \(E_F\) is the Fermi energy, \(k\) is the Boltzmann constant, and \(T\) is the temperature. The effect of temperature in Eq. (4.6) is to broaden the distribution symmetrically about the Fermi energy. This is seen in Fig. 4.3 for the molybdenum distribution taken at room temperature (~ 300° K). In addition to thermal broadening, the EDC is broadened by the resolution of the energy analyzer, which in the present case, is ~ 0.2 eV [69]. Since the broadening is symmetric about the Fermi level, differentiating the EDC, with respect to the energy, yields a minimum at the true Fermi level. In order to determine the onset, a simple linear extrapolation of the low energy electrons to zero intensity is performed. This method has been previously used for both XPS and AES [76,77] and is shown in Fig. 4.4.

The DOS in the valence band is unique for a given metal and dictates many of the macroscopic and chemical properties of the metal. For example, the electron configuration for Mo is: [Kr] 4d⁵ 5s, where the valence electrons are contained in the 4d and 5s levels and are responsible for the structure seen in Fig. 4.5. For transition metals, like Mo, the density of states is characterized by a narrow d band superimposed on a broad s-p band that extends from the Fermi level. The s-p band electrons are screened from the ion-core of the atom by the more tightly bound d- band electrons. This results in a more localized d-band and a more free-electron like s-p band [78,79].

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Fig. 4.3 (a) The Fermi edge of the photoelectron spectra for a clean (■) polycrystalline Mo surface and one exposed to 12.5 L of oxygen (○). The incident photon energy is 23 eV. (b) The derivative of the spectra at the Fermi edge. The Fermi level is given by the dotted line and corresponds to the minimum of the derivative spectra.
Fig. 4.4 The onset of photoelectron emission ($h\nu = 23$ eV) from a clean (■) Mo surface and surfaces exposed to 1.5 L (Δ) and 12.5 L (○) of oxygen. The solid lines represent the extrapolation used in determining the onset energy. The increase in onset energy with oxygen coverage indicates an increasing work function.

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4.1.3 Oxygen adsorption

The work function and the DOS are altered by oxygen coverage. This is clearly illustrated by Figs. 4.3 and 4.4, where the EDC for a clean Mo surface is compared with that for an oxygen exposed Mo surface. Because the potential difference between the detector and the surface remains constant between measurements, the Fermi levels remain fixed (Fig. 4.3). While the Fermi level remains fixed, there is an effective change in the vacuum level and so the change in the work function is determined by the change in the onset of secondary emission (Fig. 4.4). The assumption that the potential difference between the sample and the analyzer remains constant is based on the fact that the analyzer was not subject to any cleaning prior to or during the measurements. In other words, the analyzer is saturated with oxygen so that the dose incurred during the exposure does little to change the so-called contact potential of the analyzer. Table 4.1 gives the work function change, as a function of oxygen exposure, for the various metals studied.

The oxygen induced change in the DOS is seen in Fig 4.5 where new structure appears in the vicinity of 6 eV below the Fermi level which becomes more apparent if a difference spectrum is generated by subtracting the EDC for an oxygen covered surface from that for a clean surface. In Fig. 4.5, the energy scale is given in terms of the electron binding energy where the zero of this scale, \( E_{be} = 0 \), is the Fermi level. Fig. 4.5 thru Fig. 4.7 shows oxygen induced structure appearing in the vicinity of 6-7 eV below the Fermi level for the Mo, Al, and stainless steel surfaces. The difference spectra, shown in the lower panel of each figure, exhibit a decrease in the intensity near the Fermi level that accompanies the oxygen induced structure for all three surfaces.

Considering the results for Al in Fig. 4.6, the appearance of the oxygen induced peak at
Fig. 4.5 (a) Photoelectron spectra for a clean (■) Mo surface and surfaces exposed to 1.5 L (△) and 12.5 L (○) of oxygen (hv = 23 eV). The zero of the energy scale is the Fermi level. (b) The difference spectra obtained by subtracting the clean surface spectrum from the spectra for 1.5 L (△) and 12.5 L (○) of oxygen exposure.
Fig. 4.6 (a) The photoelectron spectra (hv = 23.0 eV) for a clean (■) Al surface and surfaces exposed to 51 L (○) and 103 L (△) of oxygen. (b) The difference spectra for surfaces exposed to 51 L (○) and 103 L (△) of oxygen.
Fig. 4.7 (a) The photoelectron spectra (hv = 23 eV) from a clean (■) stainless steel surface and surfaces exposed to 10 L (Δ) and 60 L (○) of oxygen. (b) The difference spectra for surfaces exposed to 10 L (Δ) and 60 L (○) of oxygen.
7 eV below the Fermi level is in good agreement with both experimental [80,81] and theoretical [82] results. This peak is ascribed to the 2p level in oxygen. The DOS should reflect changes incurred by oxygen adsorption when one considers the valence electrons in both aluminum and oxygen. The adsorption of oxygen on the surface of aluminum is described as dissociative chemisorption or, the chemical bonding of atomic oxygen to the substrate aluminum. Since oxygen is more electronegative than aluminum (electronegativities of 3.41 and 1.61 respectively), one would expect a charge transfer from the aluminum to the oxygen. In theoretical work for the chemisorption of oxygen on Al (111) by Wang et al. [82], such a charge transfer of electrons from the aluminum conduction band to the adsorbed oxygen is predicted to occur. This charge transfer occurs only near the surface such that the DOS is altered for the surface layer and little effect is seen for subsurface layers. This charge transfer also results in the depletion of the DOS near the Fermi level that accompanies the emergence of the oxygen 2p peak, and is clearly seen in Fig. 4.6.

The details of chemisorption of oxygen on other metals will vary depending on the valence structure, but as a general observation, the emergence of an oxygen induced peak at 5-8 eV and a decreased intensity near the Fermi level are the norm [83-85]. The oxygen-substrate bond, therefore, is the result of a charge transfer from the valence band of the substrate to the p-level of the oxygen atom that provides for the observed oxygen-induced change in the DOS. While a more detailed understanding of the photoemission spectra is possible, such is not relevant to the results presented in this work.
Table 4.1 The change in the work function as a function of oxygen exposure, determined by UPS, for photons with energies of 23 eV and 10 eV. For each metal, the left hand column is the oxygen exposure and the right hand column is the change in the work function. The absolute work function values determined by UPS, given at the bottom of each column, are provided as a reference. Because of the inherent uncertainty in determining these values (see text), they should only be used as a guide when considering the magnitude of the work function change.

<table>
<thead>
<tr>
<th></th>
<th>Al (poly)</th>
<th>Mo (poly)</th>
<th>Mo (100)</th>
<th>Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ex. (L)</td>
<td>Δφ (eV)</td>
<td>Ex. (L)</td>
<td>Δφ (eV)</td>
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<tr>
<td>hν = 23 eV</td>
<td></td>
<td></td>
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<tr>
<td>50</td>
<td>-0.1</td>
<td>1.5</td>
<td>+0.2</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-0.2</td>
<td>12.5</td>
<td>+1.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>tech*</td>
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<tr>
<td>hν = 10 eV</td>
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<tr>
<td>50</td>
<td>-0.1</td>
<td>1.5</td>
<td>+0.2</td>
<td>0.5</td>
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<tr>
<td>100</td>
<td>-0.2</td>
<td>12.5</td>
<td>+1.2</td>
<td>1.0</td>
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<td>φ = 4.3 eV</td>
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<td>φ = 4.6 eV</td>
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<td></td>
<td>φ = 4.7 eV</td>
<td></td>
<td>φ = 4.8 eV</td>
<td></td>
</tr>
</tbody>
</table>

* The term “tech”, meaning “technical”, is used to describe a surface for which no in situ cleaning has been performed (see chapter 5).
4.2 PHOTON-STIMULATED ION DESORPTION

4.2.1 Experiment

A "proof of principle" experiment designed to detect photon-stimulated anion desorption was undertaken to further explore the model, discussed in detail in chapter 2, which was developed to explain the results for low energy, ion-induced secondary electron and negative ion emission. While this model was developed for ion impact, it should not, in principle, be limited to such. The excitation required for ion-induced emission should also be achievable with photons of the proper resonant energy. The ion-induced O$^-$ kinetic energy distributions resulting from the excitation mechanism, shown in Fig. 2.7, exhibit a most probable kinetic energy of $\sim 1.0$ eV. This suggests that if photon-induced emission is possible, the resulting O$^-$ kinetic energy distributions should exhibit a similar most probable kinetic energy.

The experiment to search for photon-induced anion emission is not complicated and as a result, there are few variables. One variable, as noted earlier, is a magnetic field applied transverse to the symmetry axis of the CMA. This field is sufficient to drastically alter the trajectories of the electrons while only slightly affecting the anion trajectories. While this is far from an ideal detection system, it is sufficient to separate photon-induced anion emission from photoelectron emission (which greatly exceeds anion emission). Hence, the experiment is conceptually simple; measure the photon-induced emission for products with kinetic energies from 0 to 3.0 eV, from a clean and oxygen covered aluminum surface with the magnetic field on and with the field off, as a function of photon energy.
4.2.2 Results

Shown in Fig 4.8 is the photon-induced anion emission from an aluminum surface for an oxygen coverage of approximately one monolayer. This spectrum is characterized by a Gaussian distribution centered at approximately 8.7 eV with a FWHM of ~ 1 eV. The uncertainty in the photon energy is approximately the width of the points. As a confirmation that the spectrum is the result of oxygen exposure, a measurement for an adsorbate free Al surface (made prior to oxygen exposure) is also shown in Fig. 4.8. It is clear that the anion signal is present if and only if the Al substrate has been exposed to oxygen. There was no available means to verify that the negative ion emission was $O^−$.

In order to verify that the spectrum shown in Fig 4.8 is due to anions, the measurement is repeated with the magnetic field (which defocuses the photoelectrons) turned off and the results are shown in Fig. 4.9. This spectrum represents the emission of both photoelectrons and photon-induced anions and since a vast majority of the emission will be photoelectrons, the spectrum with the field off should be similar in relative intensity to the incident photon flux. The anion emission, if resonant in nature, should be independent of electron emission.

The spectrum taken with the field off is similar to the photon flux, and to a greater extent, the surface current as seen in Fig. 4.10. The surface current is a measure of all negative products leaving the surface with kinetic energies greater than zero. The spectrum with the magnetic field off, on the other hand, represents all negative products with kinetic energies between 0 eV and 3 eV. The photon flux is determined at the Ni mesh and will depend, in part, on the photoelectron yield of Ni (which will be different from that for Al). While the spectra will vary accordingly, all spectra decrease in intensity.
Fig. 4.8 Photon-stimulated anion desorption from an Al/O surface. The signal from a surface with approximately 1 ML of oxygen coverage (○) is compared to the signal from a clean aluminum surface (■). The solid line is a Gaussian function fitted to the data. The energy width of the photon energy is less than the size of the data points.
Fig. 4.9 A comparison of signals with the magnetic field off (▲), thus transmitting anions and electrons, and with the magnetic field on (○). The solid line is a Gaussian curve fitted to the data. The right ordinate refers to the count rate with the magnetic field off and the left ordinate refers to the count rate with the magnetic field on.
Fig. 4.10 A comparison of normalized signals for an Al/O surface (~ 1 ML of oxygen); the count rate with the magnetic field off (■), the surface photocurrent (Δ), and the Ni mesh photocurrent (●).

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with decreasing photon energy and none exhibit a resonance like that observed for photon-stimulated anion emission (Figs. 4.8 and 4.9).

4.2.3 Discussion

The results of Fig. 4.8 are compatible with the model for low-energy, ion-induced emission. The model invokes a collisional excitation to an antibonding state that serves as the precursor to both O\textsuperscript{−} and electron emission. As shown by Fig. 2.6, the energy difference between the AlO\textsuperscript{−} state and the antibonding (AlO\textsuperscript{−})\textsuperscript{*} state is estimated to be on the order of 7.0-8.0 eV, suggesting that photons of this energy could excite the AlO\textsuperscript{−} state in a similar manner. As seen in Fig. 4.8, the peak emission occurs for a photon energy of 8.7 eV which is in good agreement with the excitation energy derived from the model.

The reason the spectrum exhibits a finite width is the many energy states possible at the polycrystalline surface, as alluded to in chapter 2. The peak energy of the spectrum then corresponds to the most common transition and the width corresponds to a range of less frequent transitions.

Given the simple nature of this "proof of principle" experiment, anything more than a qualitative description of the process is not possible. A more extensive experiment that would provide greater detection efficiency, yield determination, anion identification, and kinetic energy measurements is needed to provide a quantitative understanding of the observed photon-stimulated anion emission. It will probably be impossible to distinguish traditional photoelectrons from secondary electrons generated via the decay of O\textsuperscript{−} on its journey to the vacuum. Nevertheless, the measurements clearly show that there exists a...
resonance, as predicted by the model for low-energy, ion-induced emission, for which the emission of O\(^+\) from an Al/O surface is possible.
CHAPTER 5

STAINLESS STEEL

302 stainless steel [86] is an Iron (Fe) based metallic alloy where the alloying components are Chromium (Cr) and Nickel (Ni). The average composition, by weight, is: 68-72% Fe, 17-19% Cr, and 8-10% Ni. In addition, trace amounts of C, Mn, P, S, and Si are normally present. 302 stainless steel is of the austenitic type and the sample studied is polycrystalline so that the surface exhibits a randomly oriented, face-centered cubic structure.

Regardless of this complex structure, oxygen-adsorbed stainless steel exhibits ion-induced emission characteristics similar to those previously found for aluminum (Chapter 2) and other metals [52]; suggesting, perhaps, some similarities in the mechanisms leading to secondary emission from stainless steel and other metals. Given these observations, it is reasonable to ask: What is the role of a complex alloy substrate, such as stainless steel, in the secondary emission process?

Understanding the interaction of low energy, positive ions with stainless steel is an important aspect of understanding environments where such interactions are common. For example, plasma discharge devices where the electrodes used, to initiate and contain the plasma, are often fabricated with stainless steel. Since all functional electrode surfaces have some form of adsorbate coverage and oxygen will, undoubtedly, be one of the
primary adsorbates, it is particularly relevant to explore how oxygen coverage effects secondary emission. In practice, however, the quantity and type of adsorbates present on a functional surface is unknown. The term “technical” has been used to describe surfaces for which no in situ cleaning has been attempted. In the canonical surface experiment, a given surface is well characterized and one typically ascertains the effects of a known amount of adsorbate. Another reasonable question then becomes: What is secondary emission from a technical surface and what, if any, is the connection to the canonical experiment? In this chapter these questions will be pursued.

In the first part of this chapter, the effect of known amounts of oxygen on the secondary electron and negative ion emission will be given and discussed in terms of the model developed in Chapter 2 for aluminum. Then, the results for ion-induced secondary emission from surfaces where the surface conditions are representative of those found in plasma discharge devices will be given. Lastly, a connection between such surfaces and an oxygen exposed surface will be explored and an example of its relevance will be discussed.

5.1 SECONDARY EMISSION: OXYGEN COVERAGE

5.1.1 Results

5.1.1.1 Yields

TOF-SIMS analysis shows that O\(^-\) is the dominant secondary ion, comprising ~ 90% of the spectrum. As would be expected, higher mass products such as FeO\(^-\) and CrO\(^-\) are also observed, but, owing to the small quantities and to poor resolution at higher mass, could not be unambiguously identified. The anion yield \((Y_{x^-})\) then is essentially O\(^-\) \((Y_{O^-})\). The secondary electron yields \((Y_e)\), for four impact energies are given in Fig. 5.1, as a
**Fig. 5.1** Absolute electron yields for Na$^+$ impacting stainless steel at 150 eV (■), 250 eV (○), 350 eV (▲), and 450 eV (Δ), as a function of oxygen exposure.

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Fig. 5.2 Absolute O\(^{\cdot}\) yields, as a function of oxygen exposure, for Na\(^{\cdot}\) impacting a stainless steel surface at 150 eV (■), 250 eV (○), 350 eV (▲), and 450 eV (△).
function of exposure and the O' yields ($Y_{O'}$) are given in Fig. 5.2 for the same conditions. $Y_c$ clearly depends upon the amount of adsorbed oxygen and appears to saturate for exposures of 10-15 L. The observed saturation of the O' emission at 10 L, observed in Fig. 5.2, is in good agreement with the results of Blasek and Weihert [88] who use the emission of O' to suggest a formation of one monolayer occurs for an exposure of 6-7 L. $Y_{O'}$ exhibits a minimum for an exposure of about 2 L and rises thereafter, saturating at approximately 10 L. Let us address the O' yield for low exposures: Annealing (which is done immediately before the yield experiments) can cause C, Mn, and S to migrate to the surface [76,87], which may combine with oxygen to form volatile compounds such as CO and SO$_2$ and subsequently desorb from the surface. Until the surface is free of these contaminates, the chemisorption of oxygen will not occur. The results of Fig. 5.2 suggest that such a "surface cleaning" may occur for an oxygen exposure of 2 L.

The electron to anion ratio, shown in Fig. 5.3, is greatly enhanced by this "cleaning". The initial increase in the ratio, below about 5 L, is not a result of a substantial increase in the electron yield but rather the decrease in ion yield. After an exposure of 5 L, the ratio is seen to increase with increasing coverage and impact energy.

In Fig. 5.4 the secondary yields are given as a function of impact energy for a clean surface and one exposed to varying amounts of oxygen. It is apparent that the presence of oxygen greatly enhances the secondary emission. This is particularly apparent at higher impact energies where the increase in $Y_{O}$ is sixfold and the increase in $Y_e$ is in excess of an order of magnitude. It is also found that a threshold exists for electron and O' emission in the vicinity of 50 eV, with the electron emission increasing substantially for impact energies greater than 100 eV.
Fig. 5.3 The electron yield to $O^-$ yield ratio, as a function of oxygen exposure, for Na$^+$ impacting stainless steel at 250 eV (O), 350 eV (▲), and 450 eV (Δ).

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Fig 5.4 (a) The absolute electron yield, as a function of impact energy, for Na⁺ impacting a clean (■) stainless steel surface and one exposed to 6 L (○) and 9 L (▲) of oxygen. (b) the absolute O⁺ yield as a function of energy for the same conditions.

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5.1.1.2 Kinetic energy distributions

The O' and secondary electron kinetic energy distributions are shown in Fig. 5.5 for an exposure of 12 L. The O' distributions exhibit a high energy, low level tail with a most probable energy of 1.5 eV. The electron spectra exhibit a similar peak at 1.5 eV and a FWHM of 1.7 eV but do not exhibit the high energy tail. With the exception of intensity, these distributions are found to be more-or-less independent of both oxygen exposure and impact energy, as illustrated by Figs. 5.6 and 5.7. The distributions for Al exhibit similar behavior (Fig. 2.3). That is to say, the electron distributions are gaussian in shape while the O' distributions exhibit a low energy peak and a low level tail at higher energies. The distributions have the same most probable energy and they are essentially independent of both impact energy and exposure. In comparison with stainless steel, the spectra for the Al substrate exhibit slightly smaller mean energies (~1 eV) and the electrons distributions have slightly smaller widths (1.0-1.5 eV).

5.1.2 Discussion

5.1.2.1 Oxygen adsorption

Owing to the ubiquity of stainless steel in a number of applications, the interaction of oxygen with stainless steel surfaces has been widely investigated. Those investigations range from the effect of alloy composition [89,90], to the manner of surface preparation [90,91], to the effect of temperature on the adsorption of oxygen [92].

There is no reason to assume the surface composition of an alloy is equivalent to that of the bulk. Indeed, it is known that both high temperature [76,87] and adsorbate coverage [93] can cause surface segregation while preferential sputtering will favor the
Fig 5.5 (a) The normalized electron (■) and O⁺ (O) for 450 eV Na⁺ impacting a stainless steel surface exposed to 12 L. (b) The normalized distributions for 250 eV and, (c) 150 eV Na⁺ impacting a stainless steel surface exposed to 12 L.

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Fig. 5.6 (a) The secondary electron kinetic energy distributions for 450 eV (■), 250 eV (○), and 150 eV (▲) Na⁺ impacting a stainless steel surface exposed to 12 L of oxygen. (b) The electron kinetic energy distributions for Na⁺ impacting stainless steel exposed to 6 L of oxygen at the same impact energies.
Fig. 5.7  (a) The O\textsuperscript{−} kinetic energy distributions for 150 eV (▲), 250 eV (○), and 450 eV (■) Na\textsuperscript{+} impacting a stainless steel surface exposed to 12 L of oxygen.  (b) The O\textsuperscript{−} kinetic energy distributions for Na\textsuperscript{+} impacting stainless steel exposed to 6 L of oxygen at the same impact energies.
removal of one component over that of another [94,95]. However, Blasek et al. [94] have shown that only slight changes in the relative surface composition of iron, chromium, and nickel results from annealing in the range of 600° to 800° C, the annealing temperature in these experiments. The chemisorption bond energies for the adsorption of oxygen on Fe, Cr, and Ni are similar [93]. This implies that, given the small difference in mass and surface binding energies, one can expect small differences in the surface concentration relative to the bulk as a result of sputter cleaning [94,95]. For sputtering conditions similar to those used here (4 keV Ar⁺), only a small surface enrichment in iron and chromium has been reported [96].

Studies of oxygen adsorption on polycrystalline iron, chromium, and nickel show similar results for the early stages of oxygen uptake. For exposures up to approximately 2 L, oxygen dissociatively chemisorbs on the surface of iron [97]. After this initial stage an oxide layer begins to form. Dissociative chemisorption on chromium is also observed for an exposure between 1 and 2 L [98]. After which, the nucleation and lateral growth of oxide islands begins. For exposures above 10 L, the formation of an oxide film is observed. Nickel is similar to chromium with the formation of oxide islands beginning at approximately 4 L [99]. The results are comparable to the extent that dissociative chemisorption, implying the formation of a metal-oxygen bond, precedes the formation of larger oxide structures.

While an alloy will have properties that are different from its constituents, it is reasonable to expect that the adsorption of oxygen on stainless steel will be similar to the interaction of oxygen with the individual components. The resistance of stainless steel to extreme oxidation and corrosion is thought to be related to its chromium
content [100,101]. To this end, many investigations have focused on the analysis of the
oxide layer formed as the result of oxygen exposures much larger than those of the present
experiments. Nevertheless, it is found that the interaction of oxygen with nickel at the
surface is minimal [88,94]. SIMS measurements [88,102] and depth profiles [76,103]
reveal large quantities of oxygen, chromium, and iron and the associated oxides at the
surface. Typically, these profiles are characterized by an outer layer rich in iron and an
inner layer rich in chromium suggesting migration of iron to the surface while chromium
accumulates at the alloy interface. Jardin et al. [76] describe the initial interaction of
oxygen with the surface to be chemisorption with chromium followed by an adsorbate-
induced reconstruction, with a migration of iron to the surface where it interacts with
oxygen. Utilizing SIMS, Blasek and Weiher [88] determine the formation of a monolayer
at 6-7 L with the second and third monolayer forming at 20 L and 50 L. The top layer is
observed to be iron rich, while the bottom is rich in chromium.

UPS experiments show that the work function of stainless steel decreases as the
oxygen coverage increases (refer to table 4.1). For an exposure of 10 L the work function
decreases by ~ 0.2 eV and for an exposure of 60 L the decrease is ~ 0.4 eV. The UPS
results also show that an oxygen-induced peak in the vicinity of 6 eV is observed in
conjunction with a decreased intensity at the Fermi level (Fig. 4.7). As mentioned in
Chapter 4, this is indicative of the charge transfer from the substrate to the adsorbed
oxygen during chemisorption. Using the results presented above it can be concluded that
oxygen is dissociatively chemisorbed on the surface prior to the formation of oxides.

Calculations by Bahrim et al. [33], discussed in chapter 2, of the energy and width of
the affinity level of O⁺ as a function of distance from an Al surface show that the
The magnitude of the affinity level is altered by that of an image potential and is greater than the work function for small distances. When the affinity level falls below the Fermi level it is energetically favorable for the vacancy in the oxygen atom to be filled by an electron from the metal, causing the adsorbed oxygen to reside on the surface as a negative ion. The ionic nature of oxygen on the surface of Al is also supported by the calculations of Wang et al. [82], as outlined in Chapter 4. While the calculations cited above were made for an Al surface, the essence of negative ion formation on a metallic substrate does not depend strongly on the substrate. This is supported by a comparison of the UPS studies of Al and stainless steel. An oxygen induced peak and a decrease in the intensity at the Fermi level are seen for both Al (Fig 4.6) and stainless steel (Fig 4.7). The results of the UPS investigations, in conjunction with the calculations of Bahrim et al. [33] and Wang et al. [82], support the formation of a stainless steel/O surface state that is similar to that described for Al, namely AlO$. In the case of stainless steel, dissociatively chemisorbed oxygen would result in the formation of surface states such as FeO$, CrO$, or NiO$.

5.1.2.2 The secondary emission model

These results for stainless steel are remarkably similar to those for Al: (1) the presence of oxygen is required for substantial secondary electron emission, (2) the dominant observed anion is $O^-$, (3) the kinetic energy distributions for the secondary electrons and $O^-$ exhibit a similar most probable kinetic energy, and (4) the kinetic energy distributions are relatively independent of the oxygen exposure and impact energy. Hence, the question of whether or not the secondary emission model, outlined in chapter 2, can be utilized to explain the results for stainless steel is a reasonable one. There are, however, numerous

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differences between Al and stainless steel. For example, the interaction of oxygen with stainless steel involves potentially three separate substrate atoms.

One important similarity is the observation that oxygen resides on the surface of stainless steel as O\(^-\) so that the formation of a molecular ions resembling FeO\(^-\), CrO\(^-\), and NiO\(^-\) would follow. For illustrative purposes a schematic diagram representing the excitation mechanism, shown in Fig. 5.8, is constructed using FeO\(^-\). This is chosen since, as seen above, Fe and its oxides are found to be the dominant species at the surface and, for illustrative purposes, more is known about the diatomic Fe-O system. To summarize this schematic, let us assume the formation of FeO\(^-\) at an equilibrium distance, \(z_{eq} \approx 3 \, \text{Å}\). This state may be collisionally excited to an antibonding state, (FeO\(^-\))\(^*\), with a probability, \(P_x(z)\), given by Eq. (2.6). After excitation, the negative ion can exit the surface and survive, or decay by electron emission either to the metal [with a width \(\Delta_m(z)\)] or to the vacuum [with a width \(\Delta_v(z)\)]. Emission to the vacuum can occur at any distance where the energy of the (FeO\(^-\))\(^*\) lies above that for FeO, while emission to the metal can occur for any distance. The latter decay channel is, by far, the dominant channel. The kinetic energy of the electron emitted to the vacuum is represented by the difference, \(\delta E_v\). In the case where the ion exits the surface and survives, its kinetic energy is represented by the difference \(\delta E_{ion}\).

The argument and calculations follow those for Al, with the parameters of the equations being adjusted to provide a fit to the experimentally observed kinetic energy distributions. The parameters used to provide the best fit are given in table 5.1. The calculated results are compared, in Fig. 5.9, with the experimental results for the kinetic energy distributions resulting from 450 eV Na\(^+\) impacting a surface exposed to 12 L of...
Fig. 5.8 A schematic diagram, similar to Fig. 2.6, of the molecular states for the interaction of Fe and oxygen on the stainless steel surface. The FeO and FeO\(^-\) ground states, as a function of distance from the surface, are isolated molecular potentials representing the atom- and ion-surface interactions. The electron decay widths are shown below the potentials. Decay to the metal and to the vacuum are represented by \(\Delta_m(z)\) and \(\Delta_v(z)\) respectively.
Fig 5.9 (a) The electron kinetic energy distribution for 450 eV Na⁺ impacting a stainless steel surface exposed to 12 L of oxygen. The observed distribution (□) and the distribution predicted by the excitation mechanism (solid line). (b) The O⁺ kinetic energy distributions for the same conditions. Shown are the observed distribution (○), the distribution predicted by the excitation mechanism (dotted line), and the distribution predicted by the collision-cascade mechanism (dashed line). The solid line is the sum of the two predicted distributions.

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Table 5.1 The parameters chosen to best fit the observed electron and O\textsuperscript{\textdagger} kinetic energy distributions for Na\textsuperscript{\textendash} impacting stainless steel/oxygen surface.

Excitation Mechanism Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>$K_i$</td>
<td>0.1 eV</td>
</tr>
<tr>
<td>$E_n$</td>
<td>0.46 eV $a_o^{-1/2}$</td>
</tr>
<tr>
<td>$b$</td>
<td>$0.2 a_o^{-2}$</td>
</tr>
<tr>
<td>$F_c$</td>
<td>0.83 eV $a_o^{-1}$</td>
</tr>
<tr>
<td>$z_{eq}$</td>
<td>3.0 $a_o$</td>
</tr>
<tr>
<td>$z_c$</td>
<td>4.8 $a_o$</td>
</tr>
<tr>
<td>$\Delta V_o$</td>
<td>0.0215 eV</td>
</tr>
<tr>
<td>$\gamma V$</td>
<td>0.119 $a_o^{-1}$</td>
</tr>
<tr>
<td>$\Delta M_o$</td>
<td>1.0 eV</td>
</tr>
<tr>
<td>$\gamma M$</td>
<td>0.9 $a_o^{-1}$</td>
</tr>
</tbody>
</table>

Collision-cascade Mechanism Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_a$</td>
<td>3.0 $a_o$</td>
</tr>
<tr>
<td>$C$</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>$U$</td>
<td>1.0 eV</td>
</tr>
<tr>
<td>$\Delta M_o$ $m_l = 0$</td>
<td>2.414 eV</td>
</tr>
<tr>
<td>$\gamma M_o$ $m_l = 0$</td>
<td>0.731 $a_o^{-1}$</td>
</tr>
<tr>
<td>$\Delta m_o$ $m_l = \pm 1$</td>
<td>3.172 eV</td>
</tr>
<tr>
<td>$\gamma M_o$ $m_l = \pm 1$</td>
<td>0.630 $a_o^{-1}$</td>
</tr>
</tbody>
</table>
oxygen (where an exposure of 12 L corresponds to a coverage of approximately one monolayer). Again, the result for the electron distribution is in good agreement with the measured result. In the case of O⁺, the result of the excitation mechanism is summed with the result from the collision-cascade to provide the best fit. The contribution from the collision-cascade mechanism represents 1/3 of the spectrum and the excitation mechanism provides the remaining 2/3.

As a further examination of the model, a calculation of the yields from the model can be accomplished using Eq. (2.20) which involves an integration of the excitation distributions shown in Fig. 5.9 over all kinetic energies. The calculated yield for the ions is

\[ Y_{\text{ion}}^{\text{ex}} = \int_{0}^{\infty} S_{\text{ion}}^{\text{ex}}(E) \, dE = 3\% \, . \] (5.1)

and for the electrons

\[ Y_{e}^{\text{ex}} = \int_{0}^{\infty} S_{e}^{\text{ex}}(E) \, dE = 12\% \, . \] (5.2)

The observed yields for the same impact energy and oxygen exposure are found to be \( Y_{O^+} \sim 0.4\% \) and \( Y_{e} \sim 5\% \). The large yield values in the model calculation arise because of the assumption that the excitation of FeO⁺ occurs with unit probability [i.e., \( \int P_{x}(z) \, dz = 1 \)], undoubtedly not the case. In order to correct this, the collisional cross section and the effective adsorption area need to be considered. Hence, the yield values should be
corrected by the factor

\[
\left( \frac{\sigma_{ex}}{A_{ad}} \right),
\]  

(5.3)

where \(\sigma_{ex}\) is the cross section for excitation and \(A_{ad}\) is the area associated with an adsorption site. While these values are not known, some reasonable assumptions can be made. If 1 monolayer is defined as \(10^{15}\) atoms/cm\(^2\) (or 0.1 atoms/A\(^2\)), then the effective adsorption area, \(A_{ad}\), would be \(10.0\) Å\(^2\). The cross sections for excitation are typically on the order of a few Å\(^2\) at these collision energies. So then, for \(\sigma_{ex} \approx 2.0\) Å and \(A_{ad} = 10.0\) Å, Eq. (5.3) becomes 0.2 for a coverage of 1 monolayer. Then, the theoretical anion yield becomes

\[
Y_{\text{ion}}^{\text{ex}} = \left( \frac{\sigma_{ex}}{A_{ad}} \right) \int_{0}^{a} S_{\text{ion}}^{\text{ex}}(E) \, dE = 0.6\% ,
\]  

(5.4)

and the electron yield becomes

\[
Y_{e}^{\text{ex}} = \left( \frac{\sigma_{ex}}{A_{ad}} \right) \int_{0}^{a} S_{e}^{\text{ex}}(E) \, dE = 2.4\% .
\]  

(5.5)

These reasonable estimates would bring the predicted yield values into remarkably good agreement with both the electron to ion yield ratio and the absolute yield values.

As a final test of the model, it is possible to examine the effect of a changing work function. In the model, the work function may be effectively varied by adjusting \(Z_{eq}\), where a lower work function corresponds to a larger \(Z_{eq}\). This is illustrated in Fig. 5.10. Experimentally, the work function may be lowered by allowing Na to accumulate on the
Fig. 5.10 (a) The electron (■) and O\(^{-}\) (○) yields, as a function of Na\(^+\) dose, for a stainless steel surface exposed to 12 L of oxygen. (b) The electron and O\(^{-}\) yields predicted by the excitation mechanism, as a function of equilibrium distance. The equilibrium distance is directly related to the work function (top abscissa). The left ordinate represents the yields by assuming the probability for excitation is unity and the right ordinate are those yields adjusted by Eq. (5.3).
surface since the accumulation of alkali metal has been shown to lower the work function [53,67,68,104]. The top panel of Fig. 5.10 illustrates the secondary electron and anion yields which result when the surface is first exposed to oxygen and then allowing Na to accumulate while simultaneously measuring the secondary electron and anion yields. The interesting observation is that the anion yield increases much faster than the electron yield as a function of sodium coverage. In fact, the magnitude of the anion yield, initially less than the electron yield, eventually surpasses the electron yield. The bottom panel of Fig. 5.10 shows that the same effect is achieved in the model calculation by increasing the metal-oxygen equilibrium position, $Z_{eq}$, or lowering the effective work function.

5.2 SECONDARY EMISSION: THE TECHNICAL SURFACE

5.2.1 Methods

A technical surface is one for which no in vacuo cleaning has been attempted or, in other words, a surface saturated with adsorbates as a result of exposure to atmosphere. Such surfaces are often used but their properties are rarely investigated. For example, stainless steel electrodes used for discharge and plasma studies are typically subject to mechanical polishing and alcohol cleaning prior to insertion into the experimental chamber. While this greatly reduces surface defects and removes oils and greases, it does not remove all of the adsorbates. In practice, most plasma discharges, after being attained, are allowed to reach an equilibrium state prior their use as processing devices or before diagnostic experiments are to be performed. During this time the interaction of charged particles with the surface proceeds and sputtering occurs (in addition to particle deposition). In addition the surface temperature is increased which will also initiate
adsorbate desorption.

In order to ascertain the secondary emission properties of electrodes in discharge devices, the surfaces, in these studies, are subject to varying amounts of surface preparation. Prior to insertion into the chamber, the surface is mechanically polished and alcohol cleaned. Such a surface is denoted as "T", a technical surface. Following insertion, the system is baked out to achieve UHV conditions and with no further in situ cleaning technical surface conditions are preserved. The ribbon may subsequently be cleaned by either resistive heating (600°C for 15 minutes) or by a combination of heating and limited argon ion sputter-cleaning. We shall denote these latter two surface conditions as "H" - heated, and "S" - sputter cleaned. The results of ion-induced secondary emission from surfaces prepared as such will be useful in understanding the secondary emission in plasma discharge devices, which is important to discharge modeling. The results will also serve as a connection between the technical surface and the well characterized surfaces discussed in Sec. 5.1.

5.2.2 Results

Shown in Fig. 5.11(a) is a TOF mass spectrum of the secondary negative ions that are sputtered from the technical stainless steel surface for an impact energy of 250 eV. It is interesting to note that the O$_2^-$ signal is larger than that for O$. The H$^-$ signal, in addition to the O$_2^-$, suggests the presence of adsorbed water on the surface and the Na$^+$ signal originates from the accumulation of Na prior to performing the TOF-SIMS experiments. The experiment requires that Na$^+$ beam focusing conditions be found after the achievement of UHV conditions so the accumulation of Na is unavoidable. Heating removes many of
Fig. 5.11 TOF-SIMS spectrum of the negative ions sputtered from stainless steel surfaces by 250 eV Na⁺. The surface conditions are: (a), a technical stainless steel surface; (b), a technical stainless steel surface that has been cleaned by resistive heating; and (c), a technical stainless steel surface that has been clean by resistive heating and limited Ar⁺ bombardment.

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the adsorbates as seen in Fig. 5.11(b) where the “H” surface reveals neither Na\(^-\) nor H\(^-\). If the surface is further cleaned with a single cycle of heating followed by sputter-cleaning, depicted in Fig. 5.11(c), the only species seen in the secondary anion spectra is O\(^-\). It is clear that removal of adsorbates by the various cleaning procedures provides a connection between the technical surface and a surfaces of the controlled experiments discussed earlier.

Absolute yields for both electrons and anions are shown in Fig. 5.12 as a function of ion impact energy for the three surface conditions. For the technical surface, anion emission is quite large and exceeds that for electron emission for almost the entire range of energies. For surface conditions H, the yields decrease considerably, but it is only after the conditions S are achieved that the electron and ion emission approaches zero. Fig. 5.13 reveals that the ratio of electrons to anions increases as the surface conditions progress from T→ H→ S. It also shows that the ratio increases with increasing impact energy for each surface condition.

The presence of alkali metals on a surface can substantially alter both the work function and emission properties for a metallic substrate [104]. With the exception of the technical surface, the integrated sodium dose to the surface is quite small and there should be no appreciable sodium accumulation on the surface during the course of the yield measurements. This is verified by a TOF-SIMS spectrum taken for surface conditions H [Fig 5.11(b)], which reveals little secondary Na\(^-\). Photoelectron work function measurements of the surface for the condition T is found to be within 1.0 eV of a clean surface (see Chapter 4) and additional measurements show the work function for the H and S surface conditions are within 0.1 eV. It can be concluded that the large variation in
Fig. 5.12 (a) Absolute secondary electron and (b) negative ion yields as a function of Na$^+$ impact energy. Shown are: (□), a technical stainless steel surface; (●), a technical stainless steel surface that has been cleaned by resistive heating; (Δ), a technical stainless surface that has been clean by resistive heating and limited Ar$^+$ bombardment; and (▼), an adsorbate-free stainless steel surface.
Fig. 5.13 The secondary electron to negative ion ratio as a function of Na$^+$ impact energy. Shown are: (□), a technical stainless steel surface; (●), a technical stainless steel surface that has been cleaned by resistive heating; and (Δ), a technical stainless surface that has been clean by resistive heating and limited Ar$^+$ bombardment.

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electron yields, observed as the surface conditions are varied, is not exclusively due to an adsorbate-altered work function.

5.3 SECONDARY EMISSION: COMPARISONS AND IMPLICATIONS

5.3.1 Comparison of Surface Conditions

The present results for secondary emission from a stainless steel surface, initiated by ion impact, clearly show that both the anion and electron yields can be quite large and depend very strongly on the incident ion energy and the surface conditions. These yields can be large even for a surface subject to heat-cleaning.

It is demonstrated that, for low secondary emission, the removal of adsorbates by sputter cleaning is required. The presence of adsorbates has a greater effect on the anion emission than on the electron emission. A comparison of Figs. 5.2 and 5.12(b), shows the anion yield for a technical surface can be more than an order of magnitude greater than that for a surface exposed to 9 L of oxygen. A similar comparison of electron yields [Figs. 5.1 and 5.12(a)] shows only a small increase in $Y_e$. The surface studies discussed in Sec. 5.2, for surface conditions similar to those found in discharge devices, are important from a practical standpoint but the dynamics of the resulting secondary emission are difficult to understand.

Several observations concerning the transition from technical to controlled surfaces are worthy of note. After heating a technical surface, the most abundant remaining secondary anion is O$^-$; and after a minimal amount of Ar$^+$ sputter cleaning, the only anion is O$^-$. This is in stark contrast to a technical surface where the O$^-$ and O$_2^-$ yields are comparable.

These observations provide a link as one progresses from a technical to a characterized...
surface, namely, a surface with a large amount of adsorbates and one exposed to a known and relatively small amount of oxygen. A comparison of those results can establish upper and lower boundaries for the resulting secondary electron and anion emission, which should be useful to researchers attempting to model plasma discharges.

5.3.2 Implications for discharge modeling and diagnostics: An example

While secondary electron emission from electrode surfaces is often included in discharge modeling, the electron yield is usually assumed to be independent of the impact energy. For example, an empirical expression for the secondary electron emission coefficient, $\gamma$, which is often used in discharge modeling, is

$$\gamma = \begin{cases} 0.016 (\text{I.P.} - 2\phi) & \text{I.P.} > 2\phi \\ 0 & \text{I.P.} < 2\phi \end{cases},$$

(5.6)

where I.P. is the ionization potential of the impacting ion and $\phi$ is the metallic work function. The above assumption implies that secondary electrons arise solely from potential emission. However, it has been shown that $\gamma$ depends strongly on both the ion impact energy and the surface coverage, features which should be considered in modeling discharges. Such considerations may be particularly important for discharge conditions where secondary electron emission plays a dominant role such as in the gamma-mode for capacitively-coupled rf discharges [105,106].

In contrast to the well-recognized importance of secondary electron emission, negative ion emission is largely neglected in the description of discharges. If anion and electron emission from electrodes are comparable, as can be the case for a technical stainless steel
Fig. 5.14 A schematic diagram of a capacitively-coupled RF discharge in oxygen. The powered electrode is connected to the RF voltage source while the opposite electrode is grounded. Depicted is the plasma, the sheath regions and the solid line is the negative ion potential. Also shown are the secondary anions generated by positive ion impact and a small hole in the ground electrode through which anions pass en route to mass and energy analysis.

surface, such an omission may compromise the accuracy of discharge simulations and diagnostic interpretations. Let us take a parallel-plate, rf discharge in oxygen, shown schematically in Fig. 5.14, as an example. Although oxygen is classified as only weakly electronegative, recent model simulations by Shibata et al. [107], for capacitively-coupled rf discharges in 0.5 Torr oxygen at 13.6 MHZ and 150 V rf voltage, indicate that the negative ion density approaches that for positive ions in the bulk plasma, with free electrons comprising only a small fraction of the total negative charge. The dominant
negative ion species is predicted to be O\(^-\) with O\(_2\)^- forming only about 2-3\% of the total negative ion density. Their results also indicate that electron attachment occurs mainly in the bulk plasma and the negative ions formed are largely trapped within the bulk plasma by the plasma sheath potentials. Consequently, the anions can not reach the electrodes and the ratio of the negative ion flux to that for positive ions at the electrode surface is predicted to be less than 10\(^{-5}\).

On the other hand, experimental observations by Zeuner et al. [108], in an rf plasma operating with conditions similar to those described above, show some seemingly contradictory results. First, O\(_2\)^- and O\(^-\) ion fluxes are found to be comparable. Secondly, the anion to cation ratio at the ground electrode increases with increasing rf voltage and is significantly higher than the prediction, ranging from 0.01 to 0.1. Ion energy analyses show that the detected negative ions have kinetic energies as high as that of the powered electrode. This behavior of the negative ions was attributed to electron attachment occurring in the sheath near the powered electrode: “A higher rf voltage causes a higher electron density, a higher ionization rate, and hence a higher positive ion current. At the same time the sheath thickness at the rf electrode is increased by the higher voltage. The combined effects of the higher electron density and a thicker sheath, where attachment processes could occur, cause a more rapid increase of the negative ion current compared to the positive ion, as can be seen from the intensity ratio [107].”

The results of Sec. 5.2 suggest that an alternative explanation for the reported large negative ion flux, viz., that the observed negative ions were secondary O\(^-\) and O\(_2\)^- anions emitted from the powered electrode due to impacting positive ions, predominantly O\(_2\)^+ in oxygen discharges. The dominant negative ion production mechanism in the bulk of an
oxygen discharge is dissociative attachment,

$$e + O_2 \rightarrow O + O^-, \quad (5.6)$$

forming $O^-$. While $O_2^-$ can form indirectly by electron transfer,

$$O^- + O_2 \rightarrow O + O_2^-, \quad (5.7)$$

which has an energetic threshold of about 1 eV, resulting in a very low $O_2^-$ formation probability for low temperature plasmas where electron energies are on the order of 1-10 eV and ion energies are, typically, 0.01-0.1 eV. The negative ions that are formed in the bulk plasma will be trapped by the sheath potentials, but the secondary $O^-$ and $O_2^-$ anions emitted from the powered electrode will have sufficient energy to penetrate the bulk plasma and overcome the sheath potential barrier near the ground electrode. The probability that secondary anion reaches the ground electrode after leaving the powered electrode may be estimated by,

$$\frac{I(x)}{I_o} = e^{-n\sigma x}, \quad (5.8)$$

where $I_o$ is the secondary anion flux leaving the powered electrode, $n$ is the number density of the parent gas ($n = P/kT$), $\sigma$ is the cross section for anion destruction, and $x$ is the electrode separation. While traversing the electrode gap, $O^-$ may be destroyed by electron transfer [Eq. (5.7)] or electron detachment,

$$O^- + O_2 \rightarrow O + O_2 + e, \quad (5.9)$$

in collisions with $O_2$. Taking a combined cross section of $8 \, \text{Å}^2$ for these two
processes [109], an electrode separation of 3 cm, and a gas pressure of 1.5 Pa (as used by Zeuner et al.), the probability that O', produced on the powered electrode, reaches the ground electrode intact can be estimated to be 0.38.

The behavior of O₂' in traversing the sheath is more complicated because of the large electron transfer cross section for low collision energies in the O₂ parent gas. Under any circumstances, the sheath potential of the powered electrode is significantly higher than that of the ground electrode [110], and thus the majority of slow O₂' ions formed in the powered sheath will again be accelerated to energies high enough to overcome the potential of the ground sheath. If we consider only the loss of fast O₂' in the bulk plasma and take the combined cross section for electron transfer and electron detachment to be 14 Å² at 200 eV [106], the probability that a fast O₂' ion will reach the ground electrode can be estimated to be 0.19.

These estimated survival probabilities for O' and O₂' (38% and 19%) would suggest that, if their emission probabilities are similar at the powered electrode, comparable intensities of atomic and molecular anions would reach the grounded electrode, a feature that has been observed [108] for the oxygen rf discharge. The negative ion yields due to impacting positive ions strongly depend on the surface conditions, ranging from negligibly small for a sputtered-clean surface to as high as 0.1 for an adsorbate-covered surface. Moreover, the negative ion identity also depends on the surface conditions. For the heat-cleaned, sputtered-cleaned, as well as oxygen-adsorbed surfaces, the secondary negative species is predominantly O'. However, for the technical surface (i.e., one which has not been subject to in vacuo cleaning), secondary O' and O₂' ions are comparable in number.

It is clearly demonstrated that if we wish to correctly model an oxygen discharge, an
understanding of the secondary emission of electrons and ions is required not only for a sputter-cleaned or an oxygen-adsorbed clean surface, but also for a surface that mimics an electrode surface immersed in a plasma.
CHAPTER 6
TUNGSTEN

Due to the fact that an adsorbate-free tungsten surface can often be achieved by heating to high temperatures, many surface techniques have been developed and tested using tungsten [111]. This, of course, leads to a wealth of information, derived from numerous techniques, concerning clean and adsorbate covered tungsten surfaces and the secondary emissions from such surfaces. Tungsten (W) has an atomic weight of 183.85, a density of 19.26 g/cc, and a melting point of 3410° C; making it one of the most durable and, hence, useful metals. This transition metal is characterized by a valence electronic structure of $4f^1 \, 5d^6 \, 6s^2$. The crystal structure is body-centered cubic and the sample used for these experiments is polycrystalline. As with aluminum and stainless steel, adsorbed oxygen enhances both the secondary electron and negative ion yields, however, as Fig. 6.1 illustrates, the negative ion emission is much different. For both aluminum and stainless steel, TOF-SIMS spectra indicate $O^-$ is the most prevalent secondary anion, comprising in excess of 90% of the spectra for all impact energies and oxygen coverages. In contrast, the TOF-SIMS spectra for 250 eV Na$^+$ impacting a tungsten surface exposed to 6 L of oxygen, seen in Fig. 6.1, clearly shows that the predominant sputtered anion is not $O^-$. 

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Fig. 6.1 TOF-SIMS analysis for anions emitted as a result of 250 eV Na$^+$ impacting a tungsten surface exposed to 6 L of oxygen. The ordinate has been changed from time to mass using Eq. (3.4) and the peak labeled WO$_x^-$ represents tungsten oxides, where $x = 2-4$ (see Sec. 6.1.3).
6.1 RESULTS

6.1.1 Yields

Unlike previous investigations, a substantial positive current is collected on lens one of the extraction stack, rendering absolute negative product yield measurements impossible. This current is found to increase with increasing impact energy, suggesting that Na$^+$ is elastically scattered from the surface. This is further justified by the following observation; if the voltage of lens one is increased such that it is similar to that of the Na source (a voltage that can retard the primary Na$^-$ beam), it is found that the positive current is eliminated. Such a voltage severely reduces the collection of negative current at the split lens and may result in the collection of secondary products, on lens one, from sources other than the W surface; it is, therefore, an unacceptable solution. For previous measurements (with lens voltages given in Fig. 3.3), it was found that the collection at the split lens represented approximately 20-25% of the total, collected negative products current and that the electron to anion ratio at the split lens is equivalent to that at lens one. For these reasons, the yields reported are the yields measured at the split lens and are taken to be an accurate reflection of the absolute yield. While not reported, the absolute yields can be estimated to be four to five times greater.

The negative secondary product yields are shown in Fig. 6.2(a) as a function of Na$^-$ impact energy. The yields are given for surface conditions ranging from clean to an exposure of 18 L of oxygen. Here again, the presence of oxygen enhances secondary emission. In Fig. 6.2(b), the ratio of electrons to anions is given as a function of impact energy. The ratio increases with impact energy and the anion emission is found to be greater than the electron emission for impact energies below ~ 300 eV.
Fig. 6.2 (a) The yield for all negative secondary products as a function of Na\textsuperscript{+} impact energy. Shown are the results for Na\textsuperscript{+} impacting a clean (■) tungsten surface and one that has been exposed to 3 L (○), 6 L (▲), and 18 L (Δ) of oxygen. The absolute yields for W are not reported but maybe estimated to be four to five times greater than those shown (see text). (b) The electron to anion ratio for the same conditions. The ratio for the clean tungsten surface is not shown.
Fig. 6.3 The total negative product (■), anion (○), and electron (▲) yields for 150 eV Na⁺ impacting a tungsten surface as function of oxygen exposure.
Fig. 6.4 The total negative product (■), anion (○), and electron (▲) yields for 250 eV Na⁺ impacting a tungsten surface as function of oxygen exposure.

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Fig. 6.5 The total negative product (■), anion (○), and electron (▲) yields for 450 eV Na⁺ impacting a tungsten surface as function of oxygen exposure.
Fig. 6.6 The electron to anion ratio for Na⁺ impacting a tungsten surface with energies of 150 eV (■), 250 eV (○), and 450 eV (▲) as a function of oxygen exposure.

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The secondary electron and anion yields as a function of exposure are given in Figs. 6.3, 6.4, and 6.5 for Na⁺ impact energies of 150 eV, 250 eV, and 450 eV. For all impact energies, the yields increase dramatically for exposures up to approximately 6 L, where they saturate. Shown in Fig. 6.6 is the electron to anion ratio. The ratios are found to decrease in value for exposures up to approximately 6 L, where the ratios reach their minimum. For an impact energy of 150 eV, the ratio is less than one for most of the exposures with a minimum value of approximately 0.3. For an impact energy of 250 eV, the ratio is greater than one for most of the exposures and minimizes at nearly 0.75. For an impact energy of 450 eV, on the other hand, the ratio is above one for most exposures with a minimum value of 3 to 4. Interestingly, the range of exposures for which the ratios decrease corresponds to the rapid increase in the yields and the ratios appear to minimize where the yields maximize.

6.1.2 Kinetic energy distributions

The normalized secondary electron and anion kinetic energy distributions resulting from the impact of 150 eV Na⁺ with a W surface exposed to 3 L, 6 L, and 18 L of oxygen are shown in Fig. 6.7. The secondary electron distributions peak at approximately 1.6 eV, have widths of nearly 2.0 eV, and are independent of exposure. The anion distributions have a low energy peak at 0.75 eV and exhibit a tail at higher energies. The peak is independent of exposure whereas the high energy tail is dependent upon exposure, diminishing with increasing exposure. The distributions resulting from 250 eV and 450 eV Na⁺ impacting a surface exposed to the same amounts of oxygen are shown in Figs. 6.8 and 6.9. For these impact energies, the electron distributions exhibit a peak energy
Fig. 6.7 (a) Normalized secondary electron kinetic energy distributions for 150 eV Na\(^+\) impacting a tungsten surface exposed to 3 L (■), 6 L (○), and 18 L (▲) of oxygen. 
(b) The normalized sputtered anion kinetic energy distributions for the same conditions.

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Fig. 6.8 (a) Normalized secondary electron kinetic energy distributions for 250 eV Na\textsuperscript{+} impacting a tungsten surface exposed to 3 L (■), 6 L (○), and 18 L (▲) of oxygen.
(b) The normalized sputtered anion kinetic energy distributions for the same conditions.

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Fig. 6.9 (a) Normalized secondary electron kinetic energy distributions for 450 eV Na\textsuperscript{+} impacting a tungsten surface exposed to 3 L (■), 6 L (○), and 18 L (▲) of oxygen.
(b) The normalized sputtered anion kinetic energy distributions for the same conditions.
Fig. 6.10 (a) Normalized secondary electron kinetic energy distributions for 150 eV (■), 250 eV (○), and 450 eV (▲) Na⁺ impacting a tungsten surface exposed to 3 L of oxygen. (b) The normalized sputtered anion kinetic energy distributions for the same conditions.
Fig. 6.11 (a) Normalized secondary electron kinetic energy distributions for 150 eV (■), 250 eV (O), and 450 eV (▲) Na⁺ impacting a tungsten surface exposed to 6 L of oxygen. (b) The normalized sputtered anion kinetic energy distributions for the same conditions.

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Fig. 6.12 (a) Normalized secondary electron kinetic energy distributions for 150 eV (■), 250 eV (○), and 450 eV (▲) Na⁺ impacting a tungsten surface exposed to 18 L of oxygen. (b) The normalized sputtered anion kinetic energy distributions for the same conditions.
between 1.9 eV and 2.2 eV and the widths are found to be approximately 2.1 eV. As before, the anion distributions have a low energy peak at 0.75 eV and a high energy tail that, again, diminishes with increasing exposure.

Figs. 6.10 - 6.12 show the distributions for impact energies of 150 eV, 250 eV, and 450 eV for surfaces exposed to equivalent amounts of oxygen. The most probable electron energy shifts by ~ 1.5 eV as the impact energy increases from 150 eV to 250 eV and 450 eV, while retaining similar widths. All anion distributions share similar low energy peaks but exhibit a tail that decreases in importance with increasing impact energy.

The distributions exhibit structure that is comparable to that observed for Al and stainless steel in the sense that the electron distributions are symmetric about the peak and the anion distributions have a low energy peak and a high energy tail. However, unlike the case for the previous substrates, the distributions are dependent on both the impact energy and oxygen exposure. For a given impact energy and coverage, the electron most probable kinetic energy differs from the anion most probable kinetic energy by, at least, 0.75 eV. Further, the anion distributions have a low energy peak that is independent of both exposure and impact energy whereas the high energy tail is found to strongly depend on both coverage and impact energy. This is in contrast to the distributions for both Al and stainless steel where the electron and O' distributions share a similar low energy peak and the distributions remain independent of both impact energy and exposure.

6.1.3 TOF-SIMS

As previously shown in Fig. 6.1, the predominant sputtered anion is not O'. This is different from what is observed for both oxygen exposed Al and stainless steel where O'
most of the negative ion emission spectrum. The dominant anion observed in the case of Na$^+$ collisions with oxygen covered tungsten is found to have a mass that is, typically, greater than 200 u. Owing to the poor resolving power at higher masses, it is not possible to unambiguously identify the broad peak observed above 200 u. However, earlier SIMS experiments have found significant amounts of tungsten-oxygen anions present in the spectra for W/O surfaces. In experiments on polycrystalline W, Benninghoven et al. [112], using a 2 keV Ar$^+$ beam, found WO$_2^-$, WO$_3^-$, and WO$_4^-$. Yu [113], investigating W(100) using 500 eV Ne$^+$, observed WO$_2^-$ and WO$_3^-$. While it is not possible to exclude WO$^-$ from the emission spectrum observed here, it is probable that the TOF-SIMS spectra is comprised of the above tungsten oxides since the masses observed are above 200 u, the mass of WO$^-$. For this reason, the higher mass products will be referred to as WO$_x^-$, where $x = 2-4$, for the remainder of the discussion.

A comparison of the area under each peak serves as method to determine the relative amount of each secondary product. When operated in the TOF-SIMS mode the EEA is set to maximize the anion intensity which corresponds to the low energy peak in the kinetic energy spectra. Analysis of the spectra reveals that, for all impact energies and exposures, the WO$_x^-$ comprises a majority of the total anion spectrum and O$^-$ comprises, at most, 20% of all anions. The ratio WO$_x^-$/O$^-$ is found to range from 3.5 to nearly 26 and increases with both increasing impact energy and exposure, confirming that the products comprising WO$_x^-$ are the dominant secondary anions at the most probable energy in the kinetic energy distribution. The EEA may be adjusted to pass higher energy anions so that TOF-SIMS can be used to identify the emission corresponding to high energy tail of the kinetic energy distribution. For these kinetic energies, the ratio WO$_x^-$/O$^-$ is between 1.5
and 5.5 and increases with both increasing impact energy and exposure. While the amount of \( \text{WO}_x^- \) always exceeds that of \( \text{O}^- \), the relative amount of \( \text{O}^- \) is greater at higher ejection energies, i.e., the tail of the kinetic energy distribution.

6.2 DISCUSSION

6.2.1 Oxygen adsorption

The tungsten ribbon is subject to prolonged annealing prior to the experiments and repeatedly annealed during the course of the experiments as part of the cleaning method. Thermal cycling of polycrystalline W surfaces has been found induce reconstruction such that much of the surface consists of (100) faces [114]. Certainly not all of the surface consists of (100) crystallites but, as will be shown, many of the results are in good agreement with previous results for W(100). For these reasons, the assumption will be made that the polycrystalline tungsten sample favors the (100) orientation and the results of both polycrystalline W and W(100) studies will be examined.

Early experiments to determine the nature of the adsorption of oxygen employed thermal desorption [115-118], electron-stimulated desorption [112,117,119], and SIMS [112,113] techniques. The abundance of desorbed tungsten oxide species led many investigators to describe the adsorption of oxygen as a two state process. The first state is related to the desorption of atomic oxygen, and the second describes the desorption of tungsten oxides. This led to the assumption that during oxygen adsorption the surface undergoes a reconstruction where oxygen penetrates the tungsten lattice [112]. On the other hand, Bauer et al. [120] argue that oxygen adsorbs on top of the W(100) surface. This is justified by the observation that the work function increases as the coverage
increases. The magnitude of the increase was in excess of 1.0 eV for a coverage of one monolayer. The argument for on-top adsorption relies on the formation of an adsorbate-substrate dipole layer at the surface where the more negative oxygen pole points outward. A negatively charged surface would prohibit electrons from leaving, thus increasing the work function. The desorption of tungsten oxides can also be described by an oxygen over layer. With increasing oxygen coverage, the tungsten-oxygen stoichiometry would increase such that the substrate tungsten atom is partially bound to multiple oxygen atoms. Such a stoichiometry would then weaken the tungsten-substrate bond so that, if sufficient energy is supplied, the desorption of tungsten-oxides may be observed. In the oxygen over layer scenario, both the observed increase in the work function and the emission of \( \text{WO}_x^+ \) in terms of increasing oxygen coverage is accounted for.

For polycrystalline W, it is found that an exposure of approximately 5 L of oxygen corresponds to a coverage of one monolayer \([115,119]\) and the formation of the second monolayer occurs for exposures on the order of 100 L \([115]\). The initial sticking coefficient is found to be unity and decreases nearly linearly with coverages up to a monolayer \([115,119]\). For W(100), an exposure of \( \sim 0.5 \) L is required for the formation of half a monolayer and exposures of 2-3 L correspond to the formation of one monolayer \([118,121,122]\). Similar exposures are required for the formation of one monolayer on W(001) and W(111) where the monolayer exposures correspond to 2-3 L \([123]\) and 6-7 L respectively \([124]\). This is in sharp contrast to W(110), where the formation of one monolayer requires exposures on the order of 1000 L \([125]\).

A measure of the emission rate as a function of substrate temperature yields information concerning the binding energy of a given species to the substrate. Thermal
desorption spectra for polycrystalline W [115-117] show that tungsten oxides desorb at a lower temperature than atomic oxygen. A similar result is found for W(100) [120] and W(110) [118]. Measurements by Lopez-Sancho and Segovia [117] for polycrystalline W determine the energy of desorption for oxygen is 4.77 eV and the average energy for the desorption of the tungsten oxides is 4.16 eV. These studies have observed that the relative emission intensity of the WOₓ⁻ anions increases with increasing coverage. Here again, the results suggest that if sufficient energy is supplied to the surface, the removal of tungsten oxide is favored over that of atomic oxygen.

These observations support the idea that the adsorption of oxygen on the surface of tungsten [considering polycrystalline W and W(100) together] can be described as chemisorbed over layers with the formation of one monolayer corresponding to 2-5 L. As the coverage increases, the stoichiometry of the adsorbate-substrate changes such that the tungsten is bound to multiple oxygen atoms which causes a weakening of the bond between the surface W and the substrate W. Oxygen adsorption results in a W-W binding energy that is less than the binding energy within the tungsten oxide.

6.2.2 Comparisons with previous results

The present TOF-SIMS measurements are in reasonably good agreement with earlier SIMS measurements made by Benninghoven et al. [112] and Yu [113] for the adsorption of oxygen on W(100). Benninghoven et al. used 2 keV Ar⁺ to induce secondary emission while Yu used 500 eV Ne⁺. Yu observed that the total anion emission intensity saturates at an exposure of ∼ 6 L (Figs. 6.3-6.5). Two notable differences, however, are that both investigators found that the O⁻ emission is greater than the WOₓ⁻ emission and the emission
of WO$_x$ exhibits a threshold exposure that is larger than that for O$^-$. In contrast, the present TOF-SIMS analysis (Sec. 6.1.3) finds WO$_x$ emission exceeds that of O$^-$ for exposures greater than or equal to 3 L. It could be that for exposures less than or equal to 3 L, this is not the case, but owing to the small signal for low exposures, this could not be determined.

Previous studies in which the secondary electron kinetic energy spectra were determined are instructive in illustrating the results of kinetic and potential electron emission. Bonanno et al. [126] found a kinetic emission threshold on the order of 3-4 keV using Xe$^+$ impacting a clean polycrystalline W surface. The kinetic energy spectra have most probable energies ranging from 2.4 to 3.7 eV for impact energies between 2 and 8 keV. The are non-symmetric with widths that increase with increasing impact energy. Hofer and Varga [127] measured the kinetic energy of secondary electrons resulting from the neutralization of slow (15 eV) Ar$^+$ near clean and oxygen covered polycrystalline W, viz., potential emission. The kinetic energy spectra have peak energies ranging from 2.5 eV, for a surface exposed to 2 L of oxygen, to 4.0 eV for a clean surface. Again, the distributions are non-symmetric, with a broadened low energy side. These results stand in contrast to the secondary electron kinetic energy distributions found in the present experiment. This is seen in Figs. 6.9 -6.11, where the electron distributions are found to be independent of oxygen coverage at a given impact energy and the peak energies shift by only 0.5 eV as the impact energy changes from 150 to 450 eV. Additionally, the widths are essentially symmetric about the peak energy. This, of course, substantiates the initial assumptions; the choice of Na$^+$, to initiate secondary emission, eliminates potential electron emission and, for impact energies up to 500 eV, renders
kinetic emission unlikely as a source of secondary electrons.

6.2.3 Discussion of results

In comparison with Al and stainless steel where O\(^-\) was, by far, the dominant secondary anion, the emission from tungsten is much different. Careful TOF-SIMS analysis indicates that the ratio WO\(_x\)/O\(^-\) is greater than unity for impact energies at or above 150 eV and for exposures greater than or equal to 3 L. This is not surprising since the desorption energy for WO\(_x\) anions has been found to be less than that for O\(^-\), implying that it requires less energy to liberate WO\(_x\) from the surface. The model used to explain low energy, ion-induced emission from Al and stainless steel was based on the observation that O\(^-\) was the dominant secondary anion. It is clear, given the large WO\(_x\) signal, that such a model cannot be applied to tungsten.

Nevertheless, the results do resemble, in some respects, those found for both Al and stainless steel. It is clear that adsorbed oxygen enhances secondary electron emission from tungsten as the yield increases with exposure. Both the electron and anion yields increase rapidly with exposure for exposures corresponding to a monolayer of adsorbed oxygen and less so for exposures greater than that. Additionally, there is qualitative agreement in the general shape of the kinetic energy spectra for aluminum, stainless steel, and tungsten.

There are, however, significant differences. The ratio Y\(_e\)/Y\(_x\) generally decreases as oxygen coverage increases, which is not the case for Al (Fig. 2.3) [49] and stainless steel (Fig. 5.3). The structure of both the electron and anion distributions depend on impact energy and exposure. The most significant difference in the kinetic energy spectra
is the difference in the electron and anion most probable kinetic energies (approximately 1.0 eV). In the case of Al and stainless steel, the electron and anion most probable kinetic energies are essentially the same and the distributions remain more-or-less independent of impact energy and exposure.

Again, the source of secondary electron emission proves problematic. The enhancement of secondary electron emission as a result of oxygen coverage cannot be explained simply in terms of an oxygen altered work function since the work function is found to increase with increasing coverage [120]. It is further demonstrated that potential [126] and kinetic [127] emission mechanisms are unlikely sources of secondary electrons, as would be expected for emission initiated by low energy Na⁺. As is the case for Al and stainless steel, there exists no structure in the kinetic energy distributions that are indicative of auto-detachment or auto-ionization. It would seem that accepted mechanisms for secondary electron emission fail to provide for the observed electron emission.

For the secondary anion emission, it is not clear if the collision-cascade mechanism can be utilized to describe the observed kinetic energy distributions. For the sputtering of O⁺, the energy distribution predicted by collision-cascade theory [Eq. (2.6)] is considered in conjunction with the probability that O⁺ survives to the vacuum [Eq. (2.4)] to predict the kinetic energy distribution [Eq. (2.8)]. The probability that O⁺ survives upon ejection into the vacuum involves the mass of oxygen and widths that are characteristic of both O⁺ and, to a lesser extent, the substrate. In order to describe the WOₓ⁺ distributions, both the mass and the characteristic widths of WOₓ⁺ are required (these are unknown). The resulting WOₓ⁺ distributions would then be summed with the O⁺ distribution in order to determine...
the total anion distribution, where the relative contributions from each distribution would vary according to both impact energy and exposure.

Since accepted theories seem to be an unlikely source of secondary emission and since the results are in qualitative agreement with the results for both Al and stainless steel, it is tempting to assume that there exists a collision-induced excitation mechanism that provides for the observed emissions. If such an excitation would occur, what is the nature of the excitation, what is the resulting emission, and does it agree with the observations? To answer these questions, let us consider and develop a model in a similar fashion to that previously developed for aluminum.

Obviously there exists a number of possible surface states, but for simplicity we shall consider two; at low exposures, the formation of WO$^-$ and, for larger exposures, the formation of W$_2$O$_3^-$. The latter state could be considered as WO$_3^-$ bound to the substrate W, where the substrate W-(WO$_3^-$) bond has been weakened, in accordance with the earlier discussion (Sec. 6.2.1). Let us now assume that a collisional excitation occurs and the WO$^-$ state desorbs as O$^-$ and the W$_2$O$_3^-$ state desorbs as WO$_3^-$. Once an anion starts its journey to the vacuum, the widths for electron emission determine if it survives to the vacuum. The electron affinity of WO$_3^-$ is 3.33 eV and for O$^-$, it is 1.5 eV. As a result, the widths for electron emission from WO$_x^-$ are probably smaller than those for O$^-$, since the electron is more tightly bound. Furthermore, one would expect a smaller electron to anion ratio for WO$_3^-$ than for O$^-$. Considering these points together, a possible description of emission arises. As the exposure increases and the surface states evolve from WO$^-$ to W$_2$O$_3^-$, the anion emission favors WO$_3^-$ which will, in turn, decrease the electron to anion ratio. As seen, the results of the experiments (Sec. 6.1) are in agreement with this
Fig. 6.13 (a) The observed (□) secondary electron kinetic energy distribution for 450 eV Na\(^+\) impacting a tungsten surface exposed to 18 L and the theoretical (—) distribution. The theoretical distribution is generated by adjusting the mass and electron decay widths within the excitation mechanism formalism to accommodate WO\(_3^−\). (b) The observed (O) anion distribution and the theoretical (—) distribution predicted by the excitation mechanism for the same conditions.

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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al (O⁺)</th>
<th>W (WO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>1.4 eV</td>
<td>1.9 eV</td>
</tr>
<tr>
<td>$K_i$</td>
<td>0.1 eV</td>
<td>0.1 eV</td>
</tr>
<tr>
<td>$E_n$</td>
<td>0.46 eV $a_o^{-1/2}$</td>
<td>0.46 eV $a_o^{-1/2}$</td>
</tr>
<tr>
<td>$b$</td>
<td>0.3 $a_o^{-2}$</td>
<td>0.2 $a_o^{-2}$</td>
</tr>
<tr>
<td>$F_c$</td>
<td>0.6 eV $a_o^{-1}$</td>
<td>0.9 eV $a_o^{-1}$</td>
</tr>
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<td>$z_{eq}$</td>
<td>3.17 $a_o$</td>
<td>2.9 $a_o$</td>
</tr>
<tr>
<td>$z_o$</td>
<td>4.35 $a_o$</td>
<td>5.5 $a_o$</td>
</tr>
<tr>
<td>$\Delta_{vo}$</td>
<td>0.0215 eV</td>
<td>0.01 eV</td>
</tr>
<tr>
<td>$\gamma_V$</td>
<td>0.119 $a_o^{-1}$</td>
<td>0.119 $a_o^{-1}$</td>
</tr>
<tr>
<td>$\Delta_{Mo}$</td>
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<td>0.5 eV</td>
</tr>
<tr>
<td>$\gamma_M$</td>
<td>0.9 $a_o^{-1}$</td>
<td>0.9 $a_o^{-1}$</td>
</tr>
</tbody>
</table>

Table 6.1 A comparison of the excitation mechanism parameters use to predict the secondary electron and sputtered anion kinetic energy distributions for Al and W. For Al, O⁺ is utilized to describe the emission and WO₃⁻ is used for W.
scenario. The relative amount of O' in the TOF-SIMS spectra is greatest for low exposures and decreases with greater oxygen coverage while the $Y_x/Y_x^+$ ratio decreases with greater coverage.

In order to calculate the kinetic energy distribution resulting from such an excitation, some assumptions must be made. The kinetic energy distributions are dependent upon the probability that the emitted anion survives to the vacuum [Eqs. (2.16) and (2.18)] which are, in turn, dependent upon mass and the decay widths [Eq. (2.9)]. Since the electron affinity of WO$_3^-$ is about twice the value of the electron affinity of O', we shall assume the width for the decay of WO$_3^-$, via electron emission, is half the value of O'. Then for the emission of WO$_3^-$, the values of $m = 232$ u, $\Delta_\omega = .01$ eV, and $\Delta_{mo} = 0.5$ eV are used to generate the kinetic energy distributions. Proceeding from these values, the calculated electron and negative ion kinetic energy distributions is fitted to the observed spectra. This is shown in Fig. 6.13, for 450 eV Na$^-$ impacting a W surface exposed to 6 L of oxygen, and the parameters are given in Table 7.1.

As seen, the kinetic energy distributions are in reasonable agreement with the observed spectra. The differences between the calculated and observed spectra are undoubtably due to the fact that only WO$_3^-$ is considered. More importantly, the calculated spectra provide for the separation of most probable kinetic energies. This separation of most probable kinetic energies is only achievable if one considers the mass and width differences together within the model. For example, the magnitude of the separation of most probable energies is not possible considering only physically plausible adjustments in the parameters for O'. A comparison of the distributions for WO$_3^-$ and O' using the same parameters (with the exception of mass and widths) is shown in Fig. 6.14(a). The parameters are chosen to
Fig. 6.14 A comparison of the results found when the theoretical electron (□) and anion (○) distributions from Fig 6.13 are modified. (a) The electron (—) and anion (…) distributions predicted by adjusting the mass and electron decay widths to agree with those of O⁻. (b) The electron (—) and anion (…) distributions predicted by adjusting only the mass to agree with that of O⁻.
most closely approximate the electron distribution and do not differ greatly from those for
Al and stainless steel. This fitting procedure illustrates that the secondary electron
emission is the result of the excitation of surface species other than that of WO⁻. In other
words, if the parameters are chosen to fit the electron kinetic energy distribution, the
largest most probable energy separation is not as large for O⁻ as it is for WO₃⁻. This is
further illustrated in Fig 6.14(b) where only different masses are considered which shows
the separation is not due simply to altered widths. Of course, widths of this magnitude are
unrealistic since the widths for O⁻ should not be equivalent to the widths for WO₃⁻.

Given the observations and the general agreement of the calculated energy
distributions, the excitation of a surface species other than WO⁻ is shown to be possible.
The nature of this species is unknown, but can be assumed to resemble W₂O₅⁻. The
observed spectra are presumed to be a complicated sum of any number of surface species
excitations and collision-cascade type distributions. Given the low resolution at higher
mass and the lack of information concerning the widths involved, the parameters required
to develop a mechanism similar to that developed previously are, at this point, unavailable.
However, it is demonstrated that such an excitation is possible and could be responsible
for the observed secondary electron emission. It is clear that more studies are required to
understand the nature of the mechanism which leads to oxygen enhanced secondary
emission from tungsten as a result of low energy, ion impact.
CHAPTER 7

CONCLUSIONS

The aim of this work was to examine low energy, ion- and photon-induced secondary emission from adsorbate covered metal surfaces. The investigations were designed with three goals in mind. The first goal was to ascertain the role of adsorbed oxygen in low energy, ion-induced secondary emission from metallic substrates. In order to accomplish this, experiments to examine such emission from oxygen covered stainless steel and tungsten have been performed. The results were analyzed within the context of a model, previously developed to explain ion-induced emission from an oxygen covered aluminum surface. The model relies on a mechanism that invokes a collisionally-induced excitation which serves as a precursor to secondary electron and O\(^{-}\) emission. While the model was developed for ion-induced emission, the mechanism should not, in principle, be limited to such. The second goal was to examine this assertion by exploring low energy, photon-induced negative ion emission from oxygen exposed aluminum to determine if such emission is possible and compatible with the predictions of the model.

The use of different oxygen-substrate systems and the demonstration that photon-induced anion emission is possible would lend further credibility to the proposed mechanism as a source of secondary electron and negative ion emission from oxygen covered metal surfaces. This is particularly important in the case of secondary electron
emission since accepted theories fail to provide for the observed emission for the parameters of the investigation, namely, low energy Na$^+$ impacting an oxygen covered surface. The choice of Na eliminates the possibility of potential emission since the ionization potential (5.1 eV) is much less than twice the work function of stainless steel ($\sim 4.7$ eV) and W ($\sim 4.3$ eV). For ion impact energies below 500 eV, kinetic emission is an unlikely source of secondary electrons.

The third goal was to investigate low energy, ion-induced secondary emission from surfaces that approximate electrode surface conditions typically found in plasma discharge environments, i.e., surfaces for which no \textit{in situ} cleaning has been performed. Since the emission of secondary electrons and negative ions resulting from plasma-surface interactions can directly effect the bulk plasma, the quantity and type of emission from such surfaces is essential to understanding plasma discharges. Because the electrodes are often fabricated from stainless steel, it is a natural choice for such studies. Secondary emissions from such surfaces have been measured and their implications toward understanding and modeling plasma discharges have been discussed.

The secondary electron and negative ion yields resulting from the impact of sodium positive ions with adsorbate covered stainless steel and polycrystalline tungsten have been measured as a function of adsorbate coverage for impact energies up to 500 eV. It is found that the electron and anion yields are dependent upon impact energy and surface coverage. The presence of adsorbates increases the electron and anion yields, regardless of the type of adsorbate, for all impact energies. With respect to secondary electron emission, the increase in emission is found to be significant; the presence of adsorbates is required for all but trivial emission levels. In order to identify the secondary anions, TOF-
SIMS measurements have been employed. In experiments where well prepared metal substrates are exposed to oxygen, the results depend on the substrate. For stainless steel, the dominant anion is found to be $O^-$ and, in the case of tungsten, the dominant anions are found to be tungsten oxides. For the experiments involving stainless steel surfaces subject to limited or no *in situ* cleaning, the anion emission depends on surface conditions. For the technical surface, the dominate anions are $O^-$ and $O_2^-$ and they are found to be comparable in number. As the surface is cleaned however, the $O_2^-$ emission decreases such that the relative yield of $O^-$ is much greater. Generally speaking then, the presence of adsorbates always increases the ion-induced secondary electron and anion emission while the relative yields and type of anion emission is dependent upon the impacting ion energy, the substrate, and the nature of the adsorbate coverage.

In addition to the yield measurements, kinetic energy distributions have been determined as a function of coverage and impact energy for well prepared, oxygen exposed surfaces. The kinetic energy distributions share similar features. For the electrons, the distributions are symmetric about low most probable energy ($\sim 1-2$ eV) with widths on the order of a couple eV. The structure of the anion distributions exhibit a similar low energy peak but are not symmetric, exhibiting a tail at higher kinetic energies. For all spectra, the distributions are relatively smooth and there exists no additional, significant structure at higher kinetic energies. The features of the distributions do depend upon the substrate, which, as noted, effects the relative yields and type of anion emission. For stainless steel, where the dominant secondary anion is $O^-$, the secondary electron and $O^-$ distributions have the same most probable kinetic energy (i.e., the low energy peak) and the distributions are found to be more-or-less independent of impact energy and exposure.
For tungsten, where the dominant secondary anion is not O', the secondary electron and anion distributions do not share a similar most probable kinetic energy and the distributions are dependent upon both impact energy and exposure.

Low energy, photon-induced negative ion emission from oxygen covered aluminum has been observed and the intensity of the emission, as a function of photon energy, has been measured. The resulting emission from an aluminum surface with about one monolayer of adsorbed oxygen shows photon-induced O' emission is possible for photons with energies less than 10 eV and is dependent upon incident photon energy such that a maximum photon-stimulated desorption of anions occurs at a photon energy of 8.7 eV.

The results of the photon-induced emission experiment directly support the model developed to explain ion-induced emission from an Al/O surface. When oxygen is chemisorbed on an aluminum surface, the oxygen resides on the surface as essentially O', forming a surface state AlO'. The model relies on the collision-induced excitation of AlO' to an antibonding state, (AlO')*, that serves as the precursor to both electron and negative ion emission. The molecular potential energy curves previously constructed to represent the Al-O surface suggests that the energy difference between the ground and excited AlO' states is on the order of 8 to 10 eV. The observed resonance in photon-induced O' emission at 8.7 eV is in remarkable agreement with this.

Ion-induced secondary electron and negative ion emission from an oxygen covered stainless steel surface is found to be similar to that for aluminum. In particular, the presence of oxygen increases the secondary electron yield and O' is the dominant sputtered anion. Furthermore, the electron and negative ion kinetic energy distributions share the same most probable energy and the distributions are essentially independent of impact
energy and oxygen exposure. Because of these similarities, it is intuitive to apply the collision-induced excitation mechanism to stainless steel. Using the appropriate parameters, the mechanism can provide for and accurately reproduce the observed emission. The mechanism is shown to duplicate the secondary electron and anion kinetic energy distributions and, provided a reasonable excitation cross section is considered, the observed absolute yields. As a proof of feasibility, the mechanism can be utilized to predict the yields as the surface work function is decreased. For such a situation, the \( \text{O}^- \) yield is predicted to increase as the work function is lowered while the electron yield is predicted to remain basically unaffected. The observed yields are, indeed, found to behave in such a manner.

The results of ion-induced secondary electron and anion emission from oxygen covered tungsten are quite different from those for stainless steel and aluminum. For W, the dominant secondary anion is not \( \text{O}^- \) and the kinetic energy distributions are dependent on both oxygen exposure and impact energy. Perhaps the most significant difference is the unequal most probable kinetic energy observed for the anions and electrons. While these differences exist, the observed secondary electron emission remains unprovided for by existing theories. It is clear that the excitation mechanism, as it was developed for aluminum and applied to stainless steel, cannot be applied to tungsten based exclusively on the observed anion emission. However, the principle of collisionally-induced excitations should not be limited to the excitation of a particular surface state, \( i.e., \) \( \text{WO}^- \). Considering the formation of a surface state other than \( \text{WO}^- \) and its subsequent excitation, proved to be in reasonable agreement with the observed emission. Using the example of \( \text{WO}_3^- \) and changing the parameters of the excitation mechanism accordingly, it is found that the
pertinent features of the kinetic energy distribution for the W/O surface could be accounted for. The parameter changes required to bring the predictions of the excitation mechanism into agreement with the observed distributions are an increase in mass and a decrease in the widths for electron emission. It is argued that since the electron affinity of WO$_3^-$ is more than twice that of O$, the widths (i.e., the decay rate) of WO$_3^-$ should be considerably less than those for O$, a physically plausible assumption. This is further substantiated by the observation that as the oxygen exposure increases the ratio $Y_e/Y_{anion}$ decreases. While the details of such an excitation requires a greater understanding, it is shown that such a scenario is possible.

A direct comparison of the model parameters for aluminum, stainless steel, and tungsten is somewhat difficult. Comparing aluminum with stainless steel, for example, requires comparing a metal and an alloy surface. However, given the interaction of oxygen with stainless steel is essentially the same as that for aluminum, the viability of the mechanism is found to be more dependent upon the nature of the metal-oxygen bond than on the particular metal substrate involved. For both aluminum and stainless steel the chemisorption of oxygen results in the oxygen residing on the surface as essentially a negative ion forming a surface state that resembles a diatomic molecular anion, viz. AlO$^-$ or FeO$^-$. For tungsten, on the other hand, oxygen adsorption studies indicate a different stoichiometry for the metal-adsorbate system where tungsten is bound to multiple oxygen atoms forming a polyatomic molecular anion. In this case, a different surface state needs to be considered.

The results of these experiments further strengthen the validity of the proposed excitation mechanism as a source of secondary electron and negative ion emission.
resulting from low energy ion impact. First, the conclusion that the excitation mechanism may be applied to different substrates, regardless of the complexity, strengthens its universality - a caveat being that the oxygen adsorption properties must be similar to that of aluminum. These results also suggest surface excitations, leading to secondary emission, maybe generalized. The excitation and desorption of more complicated surface states, in accordance with the adsorption of oxygen, are shown to be a possible source of secondary emission. Finally, the results of photon-induced O\textsuperscript{-} desorption shows that photon- and ion-induced secondary anion emission proceeds from the same mechanism, i.e., surface excitations.

For technical surfaces the secondary electron and anion emission is found to be significantly higher and decreases as the surface adsorbates are removed, an observation that is not particularly surprising. What is interesting, is that the secondary electron and anion yields are comparable as are the relative yields of O\textsubscript{2}\textsuperscript{-} and O\textsuperscript{-}. Surface cleaning, by heating or Ar\textsuperscript{-} sputtering, has a greater effect on the anion emission than on the electron emission such that, as adsorbates are removed from the technical surface, the relative O\textsubscript{2}\textsuperscript{-} yield is greatly reduced. In fact, for heating and limited Ar\textsuperscript{-} sputter cleaning, the only remaining anion present in significant quantities is O\textsuperscript{-}. This observation suggests there are similarities in emission mechanisms between the well-characterized oxygen-adsorbed surface and the uncharacterized surface subject to limited cleaning. Not only is the secondary electron emission influenced by the presence of adsorbates and the incident ion energy, the emitted anion species is also found to be dependent on the surface conditions. These observations have been largely disregarded when considering plasma and discharge modeling. It is clear that for accurate modeling, secondary emission as a result of
energetic ions impacting adsorbate covered surfaces should be considered.

While these investigations provided a greater understanding of secondary emission from adsorbate covered surfaces, much more research is needed. The excitation model is surely strengthened by showing that photon-induced anion emission is possible. A more comprehensive experiment to determine the nature of the observed anion emission would add more proof of the similarities between ion- and photon-induced emission. For example, photon-induced anion kinetic energy spectra could be utilized to distinguish the difference between a collision-cascade type distribution and an excitation type distribution. Perhaps, a more significant experiment would be the demonstration that electron-stimulated desorption of O\textsuperscript{-} from an Al/O is also possible and compatible with the predictions of the model. This would leave no doubt that low energy, ion-, photon-, and electron-induced secondary electron and negative ion emission all proceed from the same mechanism, viz., surface excitations. In the case of tungsten, a need for more details concerning the interactions between large molecular anions and surfaces is required. A better determination of the secondary anion species and the associated properties would provide for a more thorough analysis to determine if collisionally-induced surface excitations are responsible for the observed emission. If this was proven to be the case, an application of the excitation/desorption mechanism could, conceivably, be extended to a myriad of adsorbate-substrate systems.

The surface is an interesting but complicated place and the interactions of low energy, particles and photons with surfaces takes many forms. The addition of adsorbates only compounds the inherent difficulties in understanding the physics of surfaces, as exemplified by the limited success of plasma discharge models. This work has provided
some insight to the interactions at adsorbate covered surfaces, but there is much to learn. As technology advances into the realm of microstructure and microengineering, where the surface takes a more prominent role, the number of advances is matched by need for answers to some fundamental questions. None the least of which is the role of adsorbates in the secondary emission from surfaces.
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