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THE SPUTTER GENERATION OF NEGATIVE ION BEAMS:
ANALYTICAL MODELING*

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ABSTRACT

The secondary negative ion generation process is examined through the use of energy-dependent analytical models. Non-linear least squares fit parameters for the models are determined from fits to the experimental data of Yu. These models are used to illustrate the effect of work function on the energy distributions of negative ions sputter ejected from a polycrystalline molybdenum surface covered with fractional layers of cesium. Predictions are also made of the functional dependence of the probability for negative ion formation on cesium coverage.

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1. INTRODUCTION

During the past several years, considerable progress has been made toward the development of viable analytical and computer simulation models for describing processes which occur during particle bombardment of sample surfaces. For example, application of linear cascade theory in describing the chain-like momentum transfer processes which occur between energetic projectiles and atoms of a polycrystalline material has led to simple analytic formulas for estimating yields¹ and energy-angular distributions^{2,3} of sputter ejected neutral particles; the resulting formulas are able to predict the correct functional behavior, if not absolute magnitudes, for many features of the sputtering process. Computer programs, based on the Monte Carlo principle, raise the level of sophistication and accuracy of simulating a variety of projectile-target interaction phenomena. For example, programs such as those described in Refs. 4 and 5 are able to predict yields and energy-angular distributions of sputter ejected particles, ranges, spatial distributions, and projectile stopping powers within the sample, etc., which often agree with experimental observation.

The presence of minute amounts (less than one monolayer) of an alkali metal, such as cesium, on a surface greatly enhances the probability for negative ion formation of particles ejected from the surface during sputtering. Since its discovery,⁶ this phenomenon has been utilized to great practical advantage in the development of several versatile ion sources, including those described in Refs. 7-12. Sources based on this principle are widely employed to provide a variety of atomic and molecular negative ion beams for use in a growing number of applications, such as accelerator-based atomic, nuclear, and applied research, ion implantation, isotope separation, and the important analytical fields of secondary ion mass spectrometry (SIMS) and tandem mass spectrometry (TMS).

While it is true that several independent and distinct negative ion formation processes may coexist during sputtering, particularly from compound and alloyed samples, there is convincing evidence that the mechanism of formation during sputtering of "clean" metal surfaces is a form of surface ionization. The negative ion sputter formation technique is illustrated schematically in Fig. 1. Positive ion beams, usually formed by either direct surface ionization of a Group IA element or in a heavy noble gas (Ar, Kr, or Xe) plasma discharge seeded with alkali metal vapor, are accelerated to energies between a few hundred eV and several keV where they sputter a sample containing the element of interest covered with fractional layers of a highly electropositive adsorbate. A small fraction of the sputter ejected particles then leave the surface as negative ions.

While progress has been made toward a better understanding of the mechanisms underlying negative ion formation by this process, the precise mechanism continues to be debated.¹³⁻¹⁷ The key question is the role of ejection velocity in the formation process. The probability for ion formation in models based upon local thermodynamic equilibrium in the region of primary ion impact depends weakly on ion ejection velocity.^{16,17} On the other hand, theoretical treatments involving atomic excitation, leading to electron capture or loss, predict a strong velocity dependence for secondary ion emission probability.^{13,14}

In the present paper, we shall assume that the secondary negative ion formation process has the velocity dependence described by the Nørskov and Lundqvist model.¹⁴ This model then is used in conjunction with models for the neutral particle energy-angular distribution functions of Thompson² and Garrison³ to determine non-linear least squares fit parameters by fitting to the experimental data of

Yu.¹⁵ The composite model thus formed is then used to illustrate, among other things, how the negative ion formation process depends on surface adsorbate coverage.

2. THE SPUTTER NEGATIVE ION BEAM FORMATION MODEL

If we ignore collisional detachment processes and interference to sputtering of sample atoms by surface adsorbate atoms, (both effects are expected to be present at high positive ion current densities and high relative adsorbate surface coverages σ), the negative ion current I^- can be expressed by the following simple relationship:

$$I^- = 2\pi I^+ (E_1) S(E_1, \theta_i) \int_{V_i}^{E'} \int_0^{\pi/2} P^-(E_2, \theta) f(E_2, \theta) \sin\theta d\theta dE_2. \quad (1)$$

In Eq. 1, I^+ is the incident positive ion current of energy E_1 , $S(E_1, \theta_i)$ is the sputter ratio of the target at projectile energy E_1 and angle of incidence with respect to the surface normal θ_i , $f(E_2, \theta)$ is the neutral atom energy-angular distribution function and $P^-(E_2, \theta)$ is the probability for negative ion formation for atoms ejected at energy E_2 and polar angle θ with respect to the surface normal. The limits of integration over energy E_2 are taken between V_i , the image potential induced in the surface by the departing negative ion, and E' , the maximum energy transfer that can occur between a projectile of energy E_1 and mass M_1 and a target atom of mass M_2 . E' is given by the relation $E' = \frac{4M_1M_2}{(M_1 + M_2)^2} E_1$.

2.1 The Probability for Negative Ion Formation.

Nørskov and Lundqvist¹⁴ determined expressions for positive- and negative-ion emission probabilities $P^+(v_\perp)$ and $P^-(v_\perp)$ as a function of the perpendicular component of the ejection velocity of the particle with respect to the surface, $v_\perp$. For purposes of the present paper, we are only interested in $P^-(v_\perp)$.

In the prescription of Ref. 14, the probability for negative ion formation can be cast into a simple energy-dependent form given by

$$P^-(E_2, \theta) = \frac{2}{\pi} e^{-\beta \sqrt{M_2} \{ \phi(\sigma) - E_A + V_i \} / \sqrt{2E_2} \cos \theta} \quad (2)$$

where ϕ is the work function of the surface (ϕ depends on the relative adsorbate coverage σ), E_A is the electron affinity of the ejected particle of mass M_2 and energy E_2 , V_i is the image potential induced in the surface by the escaping ion, θ is the polar angle of the sputtered ion with respect to the surface normal and β is a constant. In Eq. 2, $\sqrt{2E_2/M_2} \cos \theta = v_\perp$, the component of the velocity of the escaping particle perpendicular to the metal surface. The mechanism for ion formation based on this theory is a velocity-dependent form of surface ionization. Experimental evidence in support of the velocity dependence of the secondary ion formation process has been provided by Yu for negative ions¹⁸ and Vasile for positive ions.¹⁹

2.2 The Energy-Angular Distribution Function

Under the assumption of isotropic collision cascades, and a planar surface potential E_b , linear cascade theory predicts the following energy-angular distribution function for sputter ejected atoms:²

$$f_m(E_2, \theta) = A_m \frac{E_2 \cos \theta}{(E_2 + E_b)^{3+2m}} \quad (3)$$

In Eq. 3, E_2 is the energy of the ejected particle and θ is the polar angle with respect to the normal of the surface and m is the power potential parameter. The maximum in the distribution occurs at $E_{\max} = E_b/(2-2m)$ and is independent of emission angle θ . For the low energies appropriate for sputtering, m is found to be close to zero.^{5,20} The resulting expression

$$f_0(E_2, \theta) = \frac{A_0 E_2 \cos \theta}{(E_2 + E_b)^3} \quad (4)$$

was first developed by Thompson² and is often referred to as the Thompson model.

Recent experimental results,²¹ however, show that the peak in the energy distribution shifts to lower values as the polar angle of ejection θ is increased and that the energy distribution becomes narrower at higher ejection energies E_2 . These effects are not predicted by Eq. 4. Garrison³ has introduced a modified form of Eq. 3 which is designed to account for the indicated deviations when $m = 2$ is chosen for the power potential parameter m . This equation is given by

$$f_m(E_2, \theta) = \frac{A_m E_2 \cos \theta}{(E_2 + E_b)^3} \left(\frac{E_2 \cos^2 \theta + E_b}{E_2 + E_b} \right)^{m/2} \quad (5)$$

For $m = 2$, Eq. 5 becomes

$$f_2(E_2, \theta) = \frac{A_2 E_2 \cos \theta (E_2 \cos^2 \theta + E_b)}{(E_2 + E_b)^4}. \quad (6)$$

Equation 6 has a maximum at

$$E_{\max} = E_b \frac{\left(2 \cos^2 \theta - 3 + \sqrt{4 \cos^4 \theta - 4 \cos^2 \theta + 9}\right)}{4 \cos^2 \theta}.$$

For purposes of the present study, we shall use both the Thompson² (Eq. 4) and Garrison³ (Eq. 6) expressions as representations of the sputter particle energy-angular distribution functions for $f(E_2, \theta)$ in Eq. (1). The normalization constants A_0, A_2 are determined by requiring that the integral $2\pi \int_{V_1}^{E'} \int_0^{\pi/2} f(E_2, \theta) \sin \theta d\theta dE_2 = 1$ where V_1 is the image potential induced in the surface by the departing negative ion and E' is given by $E' = 4 M_1 M_2 / E_1 (M_1 M_2)^2$. For the case where $E' = \infty$, $A_0 = 2 E_b / \pi$, and $A_2 = 3 E_b / \pi$, A_0 and A_2 are found to differ only slightly for $E' = 4 M_1 M_2 E_1 / (M_1 + M_2)^2$ for 3500 eV Ne⁺ on Mo as used in one case by Yu (Ref. 15).

3.0 Electropositive Adsorbate-Induced Work Function Changes.

It is well known that atomic adsorption of a dissimilar element on a clean surface affects the surface work function.²²⁻²⁷ The magnitude and sign of the change depends on the chemical properties of the adsorbed atom (adsorbate) and those of the host material (adsorbent). Electropositive atoms decrease the work function while electronegative atoms tend to increase the work function.

Semiempirical relations have been proposed which relate work function change $\Delta\phi$ and surface coverage σ such as those of Topping²⁸ and Gyftopoulos and Levine.²⁹ A simple analytical expression has been derived by Alton³⁰ which can be used to predict, with good accuracy, the value of the work function σ over the complete range ($\sigma = 0$ to $\sigma = 1$) of adsorbate coverage. The equation which expresses the functional dependence of ϕ on σ , can be written as follows:

$$\phi(\sigma) \approx \phi_0 + \frac{6\Delta\phi_m}{(3-\sigma_m)\sigma_m} \sigma - \frac{3\Delta\phi_m(\sigma_m+1)}{(3-\sigma_m)\sigma_m^2} \sigma^2 + \frac{2\Delta\phi_m}{(3-\sigma_m)\sigma_m^2} \sigma^3 [V]. \quad (7)$$

where ϕ_0 is the intrinsic work function of the surface at $\sigma = 0$ and $\Delta\phi_m$ is the maximum change in work function which occurs at a relative adsorbate coverage value of $\sigma = \sigma_m$. The expression which relates the maximum change $\Delta\phi_m$ in the work function at σ_m is given by

$$\Delta\phi_m \equiv -1.24 \left[\phi_0 - \frac{1}{2}(I_A + E_A) \right] [V], \quad (8)$$

where I_A is the first ionization potential and E_A the electron affinity of the adsorbate material. Expression 8 reproduces, with good accuracy, maximum work function changes observed for alkali and alkaline earth metal adsorbates.²⁹ The ability of this model to represent experimental results make it a viable candidate for use in estimating the probabilities for secondary negative ion formation during sputtering of electropositive adsorbate covered surfaces using work-function-dependent models such as described in this paper.

4.0 Computational Studies.

In a systematic experimental study of the negative ion formation process, Yu was able to simultaneously measure Mo^- yields and work function changes $\Delta\phi$ during the adsorption of cesium while bombarding clean Mo with a Ne^+ ion beam.¹⁵ Because of the limited availability of experimental data and the controlled conditions under which the experiments were conducted, the data of Yu will be used for evaluating the theoretical models considered in the present paper.

4.1 Comparison of the Theoretical Probability for Negative Ion Formation with Experiment.

Figure 2 shows fractional probability P_F^- versus relative cesium surface coverage σ which are the results of a non-linear least squares fits of the Nørskov and Lundqvist relation¹⁴ (Eq. 1) in combination with the Thompson² and Garrison³ energy-angular distribution functions $f_0(E_2, \theta)$ (Eq. 4), and $f_2(E_2, \theta)$ (Eq. 6) to the Mo^- yield versus relative Cs coverage data of Ref. 15. The normalization constants were determined as described in the text for 3500 eV Ne^+ incident on Mo, one of the conditions under which the experiments of Ref. 15 were conducted. The work-function-dependent model (Eq. 7) was used to simulate work function changes induced by cesium as measured in Ref. 15. The fits were obtained by integrating over energy E_2 between the limits $V_i = 1.4$ eV to $E' = 30$ eV, the energy band pass of the quadrupole mass filter used in Ref. 15. However, the angular acceptance of the mass filter was not indicated in Ref. 15 and thus, the limits of integration over polar angle σ were arbitrarily chosen to be between $0 \leq \theta \leq 20^\circ$. The fits displayed in Fig. 2 were obtained by using β as the free parameter at a fixed image potential $V_i = 1.4$ eV. The

absolute values for the ordinate units were also estimated from the ratio of the negative ion beam intensity to the product of positive ion beam intensity, and the sputter ratio for 3500 eV Ne⁺ incident at 45° with respect to the sample surface of Mo. As noted, the quality of fit is fairly good over the complete range of relative cesium coverage σ for both Thompson² and Garrison³ energy-angular distribution functions. Somewhat better fits to the experimental data were obtained by allowing both β and V_i to be free parameters.

4.2 Computed Negative Ion Energy Distribution Functions.

Figures 3 and 4 show the energy distributions of neutral and negative ions sputtered from a Mo surface at four surface coverages σ as determined by integrating, respectively, the Thompson² (Eq. 4) or Garrison³ relations (Eq. 5) and the product of the Thompson or Garrison relation and the Nørskov and Lundqvist¹⁴ relation (Eq. 2) over the complete range of polar angle $0 \leq \theta \leq \pi/2$. We use Eq. 7 to simulate the work function ϕ versus relative cesium coverage σ . The parameter β was obtained from the fits to the Yu data of Ref. 15 with $V_i = 1.4$ eV as discussed in Section 4.1 and displayed in Fig. 2; the electron affinity E_A and intrinsic work function ϕ_0 for Mo were used in Eq. 7 for calculating the work function ϕ at a particular cesium surface coverage σ . We note that the peaks in the negative ion energy distribution functions shift toward lower energies as the work function ϕ is lowered and reach the left most position whenever $\sigma = 0.5$; at higher relative coverages the distributions shift toward the right hand side of the energy scale. The maximum probability for negative ion formation occurs for a cesium adsorbate coverage of $\sigma = 0.5$, in keeping with the observations of Yu.¹⁵ Thus, the energy distributions of secondary negative ions in the energy-dependent prescription of Nørskov and Lundqvist are seen to be sensitive in shape and position to surface work function ϕ at adsorbate coverage σ . The effect of work function

changes on secondary ion energy spectra have been discussed, in a general sense, by Wittmack.³¹

4.3 Computed Total Probabilities for Negative Ion Formation.

In order to determine the total probability for negative ion formation at a particular surface coverage, one must integrate Eq. 1 over the complete range of particle ejection energy E_2 and over all polar angles θ . Figure 5 displays total probability P_T^- versus cesium surface coverage σ for the case when the Thompson² relation (Eq. 4) is used; Fig. 6 provides analogous results for the Garrison³ model (Eq. 6). We note that the total probability is lower at low coverages with the Garrison² model. The magnitudes of the probabilities for negative ion formation are higher by almost two orders of magnitude than those estimated from negative ion source performance data.³² The difference between the calculated values shown in Figs. 5 and 6 and the rough estimates given in Ref. 32 are, in part, due to the lack of information concerning the fraction of the total negative ion beam accepted for analysis in the experiments of Yu,¹⁵ and, in part, due to the fact that the estimates of Ref. 32 may be as much as an order of magnitude too low.

5. DISCUSSION AND CONCLUSIONS

Models now available, such as used in this paper, can, in principle, be used to quantify the secondary negative ion beam generation process. However, the limited amount of experimental data available makes it virtually impossible to evaluate the quality of a particular model for describing the process. In this paper, we have attempted to demonstrate the dependence of the velocity-dependent model on work function and to show how this model can be used to reproduce the gross features of

experimental data. The shapes and positions of the energy distribution functions, as shown in Figs. 3 and 4, are seen to be sensitively dependent on the work function ϕ or adsorbate coverage σ . This behavior is a consequence of the velocity dependence of the Nørskov and Lundqvist model. The negative ion yields of O^- ejected from V and Nb surfaces observed in the measurements reported in Ref. 18, clearly show a dependence on ejection velocity $v_{\perp} \geq 1 \times 10^6$ cm/s in agreement with the predictions of Eq. 2. However, at lower velocities, $v_{\perp} \leq 1 \times 10^6$, the yields are found to be almost independent of velocity. These findings clearly indicate that the secondary negative ion generation process is more complicated than predicted from simple velocity-dependent relations such as given by Eq. 2, at least for systems involving a highly chemically active adsorbate such as O_2 . Arguments given in Ref. 15 suggest the effect to be the result of scattering processes which occur at the surface at high adsorbate coverages. Since the effect occurs abruptly whenever the surface work function reaches its minimum where the adsorbate coverage correlates with approximately one adsorbate (cesium) atom for every eight adsorbent atoms, this seems an unlikely hypothesis. The behavior within the two distinctly different velocity regions suggests the possibility of more than one formation mechanism. Perhaps both velocity-dependent and molecular dissociation processes may contribute to the observed negative ion yields. For example, polar dissociation processes of a metal oxide (MO) might be possible when a highly vibrationally excited molecule breaks up as it leaves the surface according to $MO \rightarrow M^+ + O^-$ (polar dissociation) or dissociative attachment through collisions between a sputter ejected molecule MO and an energetic electron according to the interaction $MO + e \rightarrow M + O^-$ (dissociative attachment). These mechanisms, of course, are intended to be suggestions only. However, there is growing evidence that molecular break-up processes at the surface may be responsible for negative ion formation in negative ion sources based on the sputter principle whenever compounds are used as the sputter samples. Two examples,

among several, can be cited which lend credence to the molecular dissociation mechanism. Recently, it was found that relatively high negative ion beam intensities of Cu^- and O^- could be generated by Xe plasma sputtering of a CuO sample without the presence of an electropositive adsorbate such as cesium.¹² Effects of this magnitude are not seen during the sputtering of metal surfaces without the use of electropositive surface adsorbates. Also, methods for producing atomic negative ions from low electron affinity materials such as the Group IA elements have been developed³³ which involve the sputtering of oxides, carbonates, or other compounds containing the element of interest. The efficiency of formation using molecular compounds is found to be much higher (one to two orders of magnitude or more) than by sputtering the elemental material itself.

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Figure Captions

1. Illustration of negative ion formation by energetic particle bombardment of a metal surface covered with a fractional layer of an electropositive adsorbate.
2. Fractional probability P_F^- versus relative cesium coverage σ . The non-linear least-square fits of the product function were formed by the Nørskov and Lundqvist relation¹⁴ (Eq. 4), denoted by f_0 , and the Garrison³ relation (Eq. 6), denoted by f_2 , to the Mo^- versus cesium coverage experimental data of Yu.¹⁵ The Alton model (Eq. 7) was used to estimate the work function ϕ versus cesium coverage σ . The fitting parameter β was determined by integrating over the energy range $V_i \leq E_2 \leq E'$ where V_i was assigned a value of $V_i = 1.4$ eV and $E' = 30$ eV, the energy band pass of the quadrupole mass filter used in Ref. 15; the range of angular integration was chosen to be $0 \leq \theta \leq 20^\circ$.
3. Energy distributions of sputtered Mo neutral atoms and Mo^- ions calculated by integrating the Thompson relation² (Eq. 4) and the product of the Thompson² and Nørskov and Lundqvist¹⁴ (Eq. 2) relations over all azimuthal and polar angles, respectively. The parameter β was determined by fitting to the Mo^- versus relative cesium coverage data of Yu¹⁵ with an assigned value for $V_i = 1.4$ eV as described in the text and displayed in Fig. 2. Four relative cesium coverage values were used: $\sigma = 0.1$, $\sigma = 0.25$, $\sigma = 0.50$, and $\sigma = 0.75$. The following values were used for the electron affinity E_A , intrinsic work function ϕ_0 , and surface binding energy E_b of Mo: $E_A = 1.0$ eV; $\phi_0 = 4.27$ eV; $E_b = 6.8$ eV.
4. Energy distributions of sputtered Mo neutral atoms and Mo^- ions calculated by integrating the Garrison relation³ (Eq. 6) and the product of the Thompson² and Nørskov and Lundqvist¹⁴ (Eq. 2) relations over all azimuthal and polar angles, respectively. The parameter β was determined by fitting to the Mo^- versus relative cesium coverage data of Yu¹⁵ with an assigned value for $V_i = 1.4$ eV as

described in the text and displayed in Fig. 2. Four relative cesium coverage values were used: $\sigma = 0.1$, $\sigma = 0.25$, $\sigma = 0.50$, and $\sigma = 0.75$. The following values were used for the electron affinity E_A , intrinsic work function ϕ_0 , and surface binding energy E_b of Mo: $E_A = 1.0$ eV; $\phi_0 = 4.27$ eV; $E_b = 6.8$ eV.

5. Calculated total probability P_T^- for Mo^- formation versus relative cesium coverage σ . The total probability P_T^- was determined by integrating the product of the Nørskov and Lundqvist¹⁴ relation (Eq. 2) and the Thompson² relation (Eq. 4) over the complete energy range between $V_i \leq E_2 \leq E'$ with image potential $V_i = 1.4$ eV and E' given by $E' = 4 M_1 M_2 E_1 / (M_1 + M_2)^2$ as described in the text. The parameter β of Eq. 2 was determined by fitting to the experimental data of Yu¹⁵ as described in the text and displayed in Fig. 2. The Alton model (Eq. 7) was used to estimate the work function of the Mo surface at a particular cesium coverage σ .
6. Calculated total probability P_T^- for Mo^- formation versus relative cesium coverage σ . The total probability P_T^- was determined by integrating the product of the Nørskov and Lundqvist¹⁴ relation (Eq. 2) and the Garrison³ relation (Eq. 6) over the complete energy range between $V_i \leq E_2 \leq E'$ with image potential $V_i = 1.4$ eV and E' given by $E' = 4 M_1 M_2 E_1 / (M_1 + M_2)^2$. The parameter β of Eq. 2 was determined by fitting to the experimental data of Yu¹⁵ as described in the text. The Alton model (Eq. 7) was used to estimate the work function of the Mo surface at a particular cesium coverage σ .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6