The Sputter Generation Of Negative Ion Beams

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ABSTRACT: A brief review is given of recent progress toward a quantitative understanding of negative ion formation by sputtering from surfaces covered with fractional layers of highly electropositive adsorbates. Practical models developed for estimating changes in work functions $\Delta\phi$ by electropositive adsorbates are described. The secondary negative ion generation process is examined through the use of composite energy/velocity dependent analytical models. 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. The models predict energy distributions which are in basic disagreement with experimental observations, implying their inappropriateness for describing the sputter negative ion generation process. We have also developed a model for calculating sputter ratios based on the use of simple scaling procedures to bring Sigmund theory into close agreement with experimental observation accounting for the threshold effect. Scaling factors for projectile energies $E > 1000$ eV are found to be independent of energy while those for projectile energies $E_{th} < E < 1000$ eV were found to be energy dependent. In this study, the model and scaling techniques utilized to bring Sigmund theory into agreement with experiment are discussed in detail and several examples provided which illustrate the versatility, accuracy and utility of the model. In the present report, we describe the model and apply it to the case of sputtering a selected number of metals with energetic cesium ions. In particular, we present sputter ratio information for a number of Cs-projectile/metal-target combinations; the targets are bombarded at normal incidence to the surface and include: Be, C, Al, Si, Ti, Ni, Mn, V, Cr, Zr, Nb, Mo, Pd, Ag, Ta, W, Pt, Au, Th, and U.

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 yields [1] 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.

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. Because of this phenomenon, the sputter technique is widely used in negative ion source

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technology [6-9]. The technique is illustrated schematically in Fig. 1. The technique relies on ion bombardment of a sample containing the material of interest with positive 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. A small fraction of the sputter ejected particles leave the surface as negative ions and are accelerated from the source for experimental use.

Although several independent and distinct negative ion formation processes may coexist during sputtering, particularly from compound and alloyed samples, there is a preponderance of evidence that the mechanism of negative ion formation during sputtering of "clean" metal surfaces with low coverages of a highly electropositive adsorbate is a form of surface ionization. Of the several models which have been put forth to describe the various ion emission phenomena observed during ion bombardment of surfaces, many of which are described in Ref. 10, the velocity-dependent surface ionization model, independently derived by Blandin, Nourtier, and Hone [11], and Nørskov and Lundqvist [12], is particularly appealing because of its quantum mechanical basis. Certain experimental results lend support for this model [13,14], while others are in complete disagreement [15-17]. One of the objectives of the present study is to assess the appropriateness of this model by describing the sputter negative ion formation process.

In this report, we shall assume the validity of the Nørskov and Lundqvist relationship for the

Fig. 1. Illustration of negative ion formation by energetic particle bombardment of a metal surface covered with a fractional layer of an electropositive adsorbate.

probability for negative ion formation[12] and use it in conjunction with models for the neutral particle energy-angular distribution functions of Thompson [2] and Garrison [3] and mathematical relationships [18] for estimating changes in work function during electropositive atom adsorption, to model the negative ion generation process. The composite model thus formed is then used to illustrate, among other things, the sensitivity of the sputter negative ion formation process to changes in surface work function $\Delta\phi$. The results derived from this model are then critiqued in terms of the appropriateness of the Nørskov and Lundqvist model for describing the sputter negative ion generation process. A brief description of a new scaling technique for calculating sputter ratios from Sigmund theory [1] will

also be provided.

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:

$$I^- = 2\pi I^+(E_1) S(E_1, \theta_i) \int_{V_i}^{E_{\max}^0} \int_0^{\pi/2} P^-(E_2, \theta) f(E_2, \theta) \sin \theta d\theta dE_2 \quad (1)$$

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 ejected 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 $E_{\max}^0$, the maximum energy transfer that can occur between a projectile of energy E_1 of mass M_1 and a target atom of mass M_2 . $E_{\max}^0$ is given by the relation

$$E_{\max}^0 = \frac{4M_1M_2}{(M_1 + M_2)^2} E_1. \quad (2)$$

2.1 The Probability for Negative Ion Formation.

In the prescription of Ref. 12, the probability for negative ion formation can be cast into a simple energy-dependent form given by

$$P^-(E_2, \theta) = \frac{2}{\pi} e^{-\beta \sqrt{M_2} \{ \phi(\sigma) - E_A + V_i \} / \sqrt{2E_2} \cos \theta} \quad (3)$$

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. 1, $v_{\perp} = \sqrt{\frac{2E}{M}} \cos \theta$, 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. Equation 3 is differential and one must integrate the expression over the sputter particle energy-angular distribution $2\pi f(E_2, \theta) dE_2 \sin \theta d\theta$ to determine the total probability for negative ion formation.

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]:

$$f_m(E_2, \theta) = A_m \frac{E_2 \cos \theta}{(E_2 + E_b)^{3+2m}} \quad (4)$$

In Eq. 4, 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 $E_2 = E_{\max} = E_b/(2-2m)$ and is independent of emission angle θ . For the low energies appropriate for sputtering, m is found to be close to zero [5,19]. The resulting expression

$$f_0(E_2, \theta) = \frac{A_0 E_2 \cos \theta}{(E_2 + E_b)^3}, \quad (5)$$

was first developed by Thompson [2] and is often referred to as the Thompson model. However, experimental results 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 . Garrison [3] has introduced a modified form of Eq. 4 which is designed to account for these deviations when $m = 2$ is chosen for the power potential parameter m . This equation is given by

$$f_m(E_2, \theta) = \frac{A_m E_2 \cos \theta}{(E_2 + E_b)^3} \left(\frac{E_2 \cos^2 \theta + E_b}{E_2 + E_b} \right)^{m/2} \quad (6)$$

For $m = 2$, Eq. 6 becomes

$$f_2(E_2, \theta) = \frac{A_2 E_2 \cos \theta (E_2 \cos^2 \theta + E_b)}{(E_2 + E_b)^4} \quad (7)$$

Equation 7 has a maximum at

$$E_{\max} = E_b \frac{(2 \cos^2 \theta - 3 + \sqrt{4 \cos^4 \theta - 4 \cos^2 \theta + 9})}{4 \cos^2 \theta} \quad (8)$$

For purposes of the present study, we shall use both the Thompson [2] (Eq. 5) and Garrison [3] (Eq. 7) 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 $2\pi \int_{V_i}^{E_{\max}} \int_0^{\pi/2} f(E_2, \theta) \sin \theta d\theta dE_2 = 1$, where V_i is the image potential induced in the surface by the departing negative ion and $E_{\max}$ is given by Eq. 2. For the case where $E = \infty$, $A_0 = 2E_b/\pi$ and $A_2 = 3E_b/\pi$. A_0 and A_2 are found to differ only slightly from $E_{\max} = 4M_1 M_2 E_1 / (M_1 + M_2)^2$ for 3500 eV Ne^+ on Mo as used in one case by Yu [20].

3.0 Electropositive Adsorbate Induced Work Function Changes

Several semi-empirical relations have been proposed which relate work function change $\Delta\phi$ and surface coverage σ such as those of Topping [21] and Gyftopoulos and Levine [22]. A simple analytical expression has been derived by Alton [18] which can be used to predict with good accuracy the value of the work function $\Delta\phi$ over the complete range ($\sigma = 0$ to $\sigma = 1$) of electropositive adsorbate coverage. The equation which expresses the functional dependence of ϕ on σ , can be written as follows:

$$\phi(\sigma) \approx \phi_0 + \frac{6\Delta\phi_m}{(3-\sigma_m)\sigma_m} \sigma - \frac{3\Delta\phi_m(\sigma_m+1)}{(3-\sigma_m)\sigma_m^2} \sigma^2 + \frac{2\Delta\phi_m}{(3-\sigma_m)\sigma_m^2} \sigma^3 [V] \quad (9)$$

where ϕ_0 is the intrinsic work function of the metal at $\sigma = 0$, and $\Delta\phi_m$ is the maximum change in work function which occurs at $\sigma = \sigma_m$. The model is found to reproduce many sets of data with surprising accuracy. The ability of this model to accurately predict experimental data make it a viable candidate for use in estimating the probabilities for secondary negative ion formation during sputtering of electropositive adsorbate covered surfaces using the Nørskov and Lundqvist [12] model (Eq. 3) or other work function dependent models.

3.1 Comparison of the Theoretical Probability for Negative Ion Formation with Experiment

Fig. 2. Fractional probability P_F^- versus relative cesium surface coverage σ . The nonlinear least-square fits of the product ϕ of the Nørskov and Lundqvist relation [12] [Eq. (3)] and the Thompson relation [2] [Eq. (5)] denoted by f_0 to the Mo^- versus cesium coverage experimental data of Yu [20]. The Alton model [18] [Eq. (9)] was used to estimate the work function ϕ versus cesium coverage σ . The fitting parameter β was determined by integrating over the energy range $V_i \leq E_2 \leq E'$, $V_i = 1.4$ eV and $E' = 30$ eV, the energy band pass of the quadrupole mass filter used in Ref. [20]; the range of angular integration was chosen to be $0 \leq \theta \leq 2^\circ$.

Figure 2 shows fractional probability P_F^- versus relative cesium surface coverage σ which are the results of a nonlinear least squares fits of the Nørskov and Lundqvist relation [12] (Eq. 3) in combination with the Thompson [2] and Garrison [3] energy-angular distribution functions $f_0(E_2, \theta)$ (Eq. 5), and $f_2(E_2, \theta)$ (Eq. 7) for the Mo^- yield versus relative Cs coverage data of Ref. 20. The work-function-dependent model (Eq. 9) was used to simulate work function changes induced by cesium as measured in Ref. 20. 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, conditions used in the experiments of Yu. As noted, the quality of fit is fairly good over the complete range of relative cesium coverage σ for both Thompson [2] and Garrison [3] energy-angular distribution functions. Somewhat better fits to the experimental data were obtained by allowing both β and V_i to be free parameters.

Fig. 3. Energy distributions of sputtered Mo neutral atoms and Mo⁻ ions calculated by integrating the Garrison relation [3], Eq. (7) and the product of the Thompson [2] and Nørskov and Lundqvist [12] Eq.(3) relations over all azimuthal and polar angles, respectively. The parameter b was determined by fitting to the Mo⁻ versus relative cesium coverage data of Yu [20] with an assigned value for $V_1 = 1.4$ 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.

Fig. 4. Energy distributions of sputtered Mo neutral atoms and ions calculated by integrating the Thompson relation [2] and the product of the Thompson and Nørskov and Lundqvist [12] Eq. (3) relations over all azimuthal and polar angles, respectively. The parameter β was determined by fitting to the Mo⁻ versus relative cesium coverage data of Yu [20] with an assigned value for $V_1 = 1.4$ 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.

3.2 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 Thompson [2] (Eq. 5) or Garrison [3] relations (Eq. 7) and the product of the Thompson or Garrison relation and the Nørskov and Lundqvist [12] relation (Eq. 3) over the complete range of polar angle $0 \leq \theta \leq \pi/2$. 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 [20]. 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 . As noted, these theoretical results, derived from the velocity dependent model of Nørskov and Lundqvist [12], predict wide energy distributions (several tens of eV) with the maxima peaked at a few to several tens of eV from the origin (zero of energy). These results are in disagreement with experimental observations of Doucas [15,16] and more recently by Nakamura, et al., [17] where the maxima in the energy distributions are observed to be peaked a few eV from the origin, with widths more in keeping with those theoretically predicted by the Thompson [2] or Garrison [3] models and experimentally measured for neutral sputtered particles [25].

3.3 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 Thompson [2] relation (Eq. 5) is used: Fig. 6 provides analogous results for the Garrison [3] model (Eq. 7). We note that the total probability is lower at low coverages with the Garrison model.

4.0 The Scaled Sigmund Theory Model

The sputtering ratio or yield, i.e., the number of atoms ejected from a surface per incident ion, depends on a number of parameters of the interacting projectile-target combination, including projectile energy and angle of incidence with respect to the surface normal of the material in question and the atomic numbers and atomic masses of the projectile and target. These dependencies have been incorporated in theoretical treatments of the sputter process and are, therefore, fairly well understood. Other parameters such as the dependency of the sputter ratio on the topography of the sample surface and on dose are less well understood and are not readily amenable to theoretical

Fig. 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 Lundqvist relation [12] [Eq. (3)] and the Thompson relation [2] [Eq. (5)] over the complete energy range $V_i \leq E_2 \leq E'$ with image potential $V_i = 1.4$ eV and E' given by $E' = 4M_1M_2E_1/(M_1 + M_2)^2$ as described in the text. The parameter β of Eq. (3) was determined by fitting to the experimental data of Yu [18] as described in the text and displayed in Fig. 2. The Alton model of Eq. 9 was used to estimate the work function of the Mo surface at a particular cesium coverage σ .

Fig. 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 Lundqvist relation [12] [Eq. (3)] and the Garrison relation [2] [Eq. (5)] over the complete energy range $V_i \leq E_2 \leq E'$ with image potential $V_i = 1.4$ eV and E' given by $E' = 4M_1M_2E_1/(M_1 + M_2)^2$ as described in the text. The parameter β of Eq. (3) was determined by fitting to the experimental data of Yu [18] as described in the text and displayed in Fig. 2. The Alton model of Eq. (9) was used to estimate the work function of the Mo surface at a particular cesium coverage σ .

treatment. The sputter model derived by Sigmund includes most of the fundamental parameters [1].

In the Sigmund theory, the energy of an ion slowing down in a target is dissipated by means of elastic and inelastic collisions with target atoms near the surface, and dissipated further in elastic target-atom-target collisions. The transport of kinetic energy in such atomic collision cascades is treated on the basis of the Boltzmann equation; the principal physical input parameter in the theory is an ion-atom and atom-atom potential of Thomas-Fermi type. The intersection of the collision cascade with the target surface determines the sputter yield as well as the angular and energy distributions of sputtered atoms. For an isotropic target, the energy distribution goes approximately according to E^{-2} over a wide range of ejected-atom energies, and the angular distribution of ejection is approximately cosine. The theoretical model is based on solution of the Boltzmann transport equation and the use of linear cascade theory to simulate a sequence of elastic collisions set in motion beneath the surface of a solid or liquid by an energetic projectile as it slows down in a homogeneously distributed matrix. The cascades are initiated by projectile energy transfer to lattice atoms, freeing them from their sites and setting them in motion. These energetic atoms, in turn, have collisions with other atoms creating a cascade of recoils. As the cascade develops, some of the recoiling atoms reach the surface with sufficient energy to escape the surface potential energy barrier and are said to be sputtered. By solving the Boltzmann equation, Sigmund was able to derive analytical formulas for estimating sputter ratios. Despite the universal appeal of an analytical approximation such as provided by the Sigmund model, sputter ratio values derived from the theory often differ from experimental values by factors up to five, depending on the projectile target combination and the energy regime over which the sputtering takes place. The original Sigmund theory takes the form

$$S_s(E, \theta) = \frac{3\lambda\alpha E}{4\pi^2 U_0 (\cos \theta)^F} \quad (\text{for } E \leq 1000 \text{ eV}) \quad (10)$$

$$S_s(E, \theta) = \frac{0.042\alpha S_n(E)}{U_0 (\cos \theta)^F} \quad (\text{for } E > 1000 \text{ eV}) \quad (11)$$

where

α is a tabulated function of the ratio of the target mass M_2 to projectile mass M_1 ,

U_0 is the heat of sublimation of the target,

θ is the angle between the incident projectile and the surface normal,

F usually has values between 1 and 1.7, depending on the ratio of target to projectile mass.

$$\lambda = 4 M_1 M_2 / (M_1 + M_2)^2,$$

$$S_n(E) = 4\pi Z_1 Z_2 e^2 a_{12} [M_1 / (M_1 + M_2)] S_n(\epsilon),$$

Z_1, Z_2 are the respective projectile and target atomic numbers,

$$a_{12} = 0.8853 a_0,$$

a_0 is the radius of the first Bohr orbit,

$S_n(\epsilon)$ is the projectile stopping power in the target, and

$$\epsilon = \frac{a_{12} M_2 E}{Z_1 Z_2 e^2 (M_1 + M_2)} \quad (12)$$

In this formulation, we incorporate the approximation determined by Wilson et al. for the stopping power [23],

$$S_n(\epsilon) \equiv \frac{1/2 \ln(1 + \epsilon)}{\epsilon + 0.14\sqrt{\epsilon}} \quad (13)$$

This is supposed to be applicable in both the low- and high-energy regimes and, therefore, permits the use of a single equation for estimating sputter ratios. Using this equation for the stopping power, the Sigmund theory becomes:

$$S_s(E, \theta) = \frac{0.042 \alpha S_n(E)}{U_0 (\cos \theta)^F} \quad (\text{for } E > 0) \quad (14)$$

However, we found it necessary to use separate scaling techniques for the low ($E_{th} \leq E \leq 1000$ eV) and high ($E > 1000$ eV) energy regimes of the projectile. The scaled form of the Sigmund theory then takes on the following forms:

$$S(E, \theta) = A_1(E) S_s(E, \theta) \quad (\text{for } E_{th} \leq E \leq 1000 \text{ eV}) \quad (15)$$

$$S(E, \theta) = A_2 S_s(E, \theta) \quad (\text{for } E > 1000 \text{ eV}) \quad (16)$$

where E_{th} corresponds to the threshold energy required to effect sputtering.

Good agreement was found over the complete high-energy regime between Sigmund theory and experiment, with the approximation of Eq. (13) used for $s_n(\epsilon)$, by linearly scaling Eq. (16) by a factor A_2 . Two methods are used to determine A_2 : A_2 can either be determined from experimental data for projectile energies $E \geq 1000$ eV or by least squares fits to experimental sputter ratio versus projectile atomic number data for a given energy and particular target material, again at projectile energies $E \geq 1000$ eV. In either case, the scaling parameter A_2 is derived by determining the sputter ratio for the projectile of interest and dividing it by the unscaled Sigmund theory value. The latter technique can be used to obtain scaling parameters for projectiles interacting with a specific target for which there is no known sputter ratio information. However, sputter ratio information at the chosen energy must be available for a few projectiles so that a least squares fit to the data can be obtained. The sputter ratio information for the projectile of interest can be derived and this information then used to determine the scaling factor.

The scaling factor A_1 , in general, was not found to depend on projectile energy E for the high-energy case (for $E > 1000$ eV). This was not the case for projectile energies $E_{th} \leq E \leq 1000$ eV. A function $G(E)$ was found to be necessary in order to bring Eq. (12) into agreement with experiment. For this energy regime, G was found to depend on the energy of the projectile E in the following way:

$$G(E) = a_0 + a_1(E) + a_2(E)^2 + a_3(E)^3 + a_4(E)^4 \quad (17)$$

The constants a_i are averages derived from linear least squares fits to several sets of experimental data for neon, argon, krypton, and xenon projectiles interacting with a variety of targets over the low-energy regime $E_{th} < E \leq 1000$ eV. The function $G(E)$ is required to have a value of unity at 1000 eV.

Fig. 7. Comparisons of the normalized function $G(E)$ derived from least squares fits to many sets of projectile/target experimental data with least squares fits to normalized neon projectile/Mo target sputter data. The experimental data for both functions were taken from the compilations of Ref. [24].

Fig. 8. Comparison of the normalized function $G(E)$ derived from least squares fits to many sets of projectile/target experimental data with least squares fits to normalized krypton projectile/Pt target data. The experimental data for both functions were taken from the compilations of Ref. [24].

A_2 is then used as a linear scaling factor for both the low- and high-energy regimes, so that $A_1(E) = G(E) A_2$.

The function $G(E)$ was determined by least squares fits to many sets of projectile/target sputter data, taken from Ref. [24]. Figures 7 and 8, respectively, display least square fits to Ne projectile/Mo target sputter data and Kr projectile/Pt sputter data, normalized to unity at 1000 eV. As noted, the two normalized curves are in close agreement with experimental data and are typical of the agreement found between many other projectile/target combinations with the function $G(E)$. A limited number of threshold energy values E_{th} are available in the literature (Ref. [25]). For cases where no value E_{th} is available, a value of $E_{th} = 24$ eV is used, which is an average of the values reported in Ref. [25].

4.1. Comparisons of sputter ratios calculated by use of Sigmund and scaled Sigmund theory with experimental data

Examples of the sputter ratio S versus Cs projectile energy, as calculated by use of Sigmund and scaled Sigmund Theory, are shown in Figs. 9-28. Experimental data, where available, are also shown for comparison. As noted, the scaled theory agrees substantially better with available experimental data than unscaled theory for all cases considered. This is found to be true, in general.

Fig. 9. Sputter ratio as a function of energy for Cs projectiles on a Be target.

Fig. 10. Sputter ratio as a function of energy for Cs projectiles on a C target.

Fig. 11. Sputter ratio as a function of energy for Cs projectiles on an Al target. Experimental data taken from the compilations of Ref. 24.

Fig. 12. Sputter ratio as a function of energy for Cs projectiles on an Si target.

Fig. 13. Sputter ratio as a function of energy for Cs projectiles on a Ti target. Experimental data taken from compilations of Ref. 21.

Fig. 14. Sputter ratio as a function of energy for Cs projectiles on a Ni target.

Fig. 15. Sputter ratio as a function of energy for Cs projectiles on a Mn target.

Fig. 16. Sputter ratio as a function of energy for Cs projectiles on a V target.

Fig. 17. Sputter ratio as a function of energy for Cs projectiles on a Cr target.

Fig. 18. Sputter ratio as a function of energy for Cs projectiles on a Zr target.

Fig. 19. Sputter ratio as a function of energy for Cs projectiles on a Nb target. Experimental data taken from the compilations of Ref. 24.

Fig. 20. Sputter ratio as a function of energy for Cs projectiles on a Mo target.

Fig. 21. Sputter ratio as a function of energy for Cs projectiles on a Pd target.

Fig. 22. Sputter ratio as a function of energy for Cs projectiles on an Ag target.

Fig. 23. Sputter ratio as a function of energy for Cs projectiles on a Ta target.

Fig. 24. Sputter ratio as a function of energy for Cs projectiles on a W target. Experimental data taken from the compilations of Ref. 24.

Fig. 25. Sputter ratio as a function of energy for Cs projectiles on a Pt target.

Fig. 26. Sputter ratio as a function of energy for Cs projectiles on an Au target.

Fig. 27. Sputter ratio as a function of energy for Cs projectiles on a Th target.

Fig. 28. Sputter ratio as a function of energy for Cs projectiles on a U target.

5.0 Conclusions

Considerable progress has been made toward the understanding of the mechanisms involved in negative ion formation during sputtering. Based on the results of this study, velocity dependent models such as that of Nørskov and Lundqvist [12] (Eq. 3) for the probability of negative ion formation would appear to be inappropriate for describing the sputter-negative ion formation process. It would appear that other models, less sensitive to velocity would be more appropriate. These models, in combination with the Alton model [18] for estimating work function changes during electropositive atom adsorption, could be used in combination with the scaled Sigmund theory for sputtering, to predict probabilities and energy distributions of negative ion beams formed during sputtering. From these studies, it is clear considerably more experimental work needs to be performed in order to select and fine tune other less velocity dependent theoretical models and to assess in depth their validity for estimating the probability for negative ion formation during sputtering from surfaces covered with fractional layers of electropositive adsorbates. Research sponsored by the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract number DE-AC05-96OR22464.

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