A model, which assumes that chemisorption is the dominant mechanism, is applied to the sputtering rate measurements of the screen grid of a 30 cm thrust ion thruster in the presence of nitrogen. The model utilizes inputs from a variety of experimental and analytical sources. The model of environmental effects on sputtering was applied to thruster conditions of low discharge voltage and a discussion of the comparison of theory and experiment is presented.
SPUTTERING IN MERCURY ION THRUSTERS

Maria A. Mantenla & and Vincent M. Rauline
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

Abstract

Ground based tests of Hg ion thrusters have identified sputter-erosion of thruster components as one of the main life limiting phenomena. Subsequent measurements have revealed that sputtering rates can be affected by background gases at pressures as low as 10^{-7} torr. With the recent interest in thin film technology, sputtering in the presence of reactive gases has been studied in great detail. This paper presents the results of many of those studies and applies them to the sputtering of electric thrusters. A model, which assumes that desorption is the dominant mechanism, is applied to the sputtering rate measurements of the screen grid of a 30-cm thruster in the presence of nitrogen. The model utilizes inputs from a variety of experimental and analytical sources. The model of environmental effects on sputtering was applied to thruster conditions of low discharge voltage and a discussion of the comparison of theory and experiment is presented.

Introduction

Ground based life tests of mercury ion thrusters have identified sputter-erosion of thruster components as one of the main life limiting phenomena. Subsequent measurements have shown that thruster component sputtering can be affected by background gases at pressures as low as 1x10^{-7} torr. This effect is a consequence of the results of ground and space tests very difficult.

The reduction of sputtering rates due to background plasma has been previously recognized and applied to thruster tests and data from other sources will be presented. A brief review of the results of background gases on sputtering is then presented followed by a discussion of a model of sputtering phenomena in the presence of background gases. Comparisons are then drawn between the models and the results obtained in a 30-cm mercury ion thruster.

Effects of Background Gases on Sputtering

M. Mantenla & and V. Rauline

Reference 3 describes the effect of background residual gases on sputtering rates of the ion optics screen grid of a mercury ion thruster as determined from direct grid thickness and molybdenum spectral intensity measurements. Figure 1 (from ref. 3) shows the sputtering rates from grid measurements operated in two different facilities as a function of test facility pressure. The facility pressure was determined from the temperature of the cold wall and the gas pumping speed for the particular tests. For discharge chamber voltages between 35 and 37 volts, a large decrease of the screen grid sputtering rate is observed with increasing facility pressure. At a discharge voltage of 32 volts, the sputtering rate is considerably reduced at given pressure due to a decrease of ion energy as well as a reduction of multiply charged ions in the thruster.

Figure 2 shows the spectral intensity of atomic molybdenum which was sputtered from the screen grid, as a function of nitrogen pressure. Nitrogen was introduced directly onto the facility beginning at the no load pressure of about 1x10^{-7} torr. Nitrogen was chosen for the test because of its availability and the fact that in this facility at no load conditions, it was found to be the most abundant single species of the residual gases (ref. 1). Data are shown for discharge voltages of 40, 45, and 50 volts. As the nitrogen pressure increased (Fig. 2) there is a decrease in the molybdenum spectral line (HOL) intensity associated with sputtered screen grid material. Similar trends in the direct sputtering rate measurements were observed as the facility pressure was varied (Fig. 1).

As pointed out in ref. 3, the observed molybdenum spectral intensity is expected to be proportional to the sputtering rate of the screen grid if the thruster plasma conditions are held constant. Assuming the plasma density, electron temperature, plasma spatial distributions, and charge state of the ions are negligible affected by the background pressure, the spectral intensity of line 2 should be proportional to the sputtering rate for a given discharge voltage. This assumption was verified in Ref. 3 as spectral intensities of neutral and ionized mercury were found to be essentially constant with nitrogen pressure up to the low 10^{-3} torr range.

Figure 2 shows that the molybdenum spectral intensity increases substantially as the discharge voltage is raised from 40 to 50 volts. Because the plasma conditions are dependent on the discharge voltage, the spectral intensity cannot be correlated directly to the sputtering rate for different discharge voltages. It is clear, that at the 50-volt condition the Hol line intensity and thus the sputtering rate of the screen grid reaches a plateau around the 2x10^{-7} torr level. This plateau represents the "clean metallic surface" or simulated space condition at a discharge voltage of 45 volts. It is not certain if a plateau has been reached at 40 volts and below, a plateau is not reached. Therefore, the sputtering rates of a 30-cm thruster operating at normal conditions of discharge voltage of 32 volts are affected by background gases because pressures less than 1x10^{-7} torr are not readily available for thruster tests.
It should be pointed out that the spectral data of Ref. 3 was plotted as a function of the partial pressure of nitrogen, but may also include effects due to other gases which have been found to be reactive.\(^1\) Therefore, it was decided to plot the total facility pressure, rather than the partial pressure of nitrogen, for all data presented herein. At the higher pressures, the effect of the other gases becomes negligible.

In order to show the effect of background gases as a function of ion energy, the screen grid was biased negatively, with respect to its normal cathode potential. Based on the results of tests, the electrical parameters and spectral analysis of the thruster discharge, the screen grid did not significantly perturb the plasma conditions. The results of these tests, shown in Fig. 3 (from Ref. 3), were taken at a discharge voltage of 50 volts and an ion current of 2 A. Here the spectral line intensity was normalized to the maximum intensity for each bias test. The data show that the curve is shifted slightly to the right or higher pressure with increasing ion energy.

These data will be subsequently used in the section dealing with the sputtering model.

Review of Environmental Effects on Sputtering Rates

The sputtering characteristics shown in Figs 1 to 3 are similar to those observed by others studying the effects of reactive gases. Data which evaluated the sputtering rate directly\(^8,13,14,16\) and those that inferred sputtering rates by measuring deposition rates\(^1,11,12\) are found in literature. Typical curves for these references are shown in Fig. 4 for various combinations of ion type, ion energy, and target material. It is observed that the magnitude of the change of the sputtering rate with pressure ranges from about a factor of 10 (similar to results observed in thrusters with a Mo-N system) to no change at all for Au and Ag-Ox systems. The latter result is similar to that obtained in the thruster tests with increasing argon and mercury background pressure. It should be pointed out that deposition data usually underestimate the magnitude of the change of the sputtering rate of the metal target.

As shown in Fig. 4, the effect has been reported in the literature at pressures considerably higher than those found in Figs 1 to 3. This is most probably due to the higher energy of the ions employed in those studies. To obtain a more exact comparison the ion current density also has to be considered. Increasing the current density shifts the curve toward higher pressure, at a given ion energy.\(^9,11\)

Another parameter of interest is the pressure range over which the change in sputtering rate takes place. In the 30-cm thruster (Figs 1 to 3) the sputtering rate decreased over two orders of magnitude of pressure. In some tests (Fig 4), the sputtering rate variation occurred over a very narrow pressure range, in a nearly step-like fashion. As will be discussed later, this difference may be due to the differences in the degree of reactivity between the target surface and the background gas.

Interactions of Gases with Metals

The adsorption of gas by metals is due to a field force at the surface of the solid, which attracts the gas. The forces of attraction may be physical or chemical and the terms physisorption and chemisorption are generally used to distinguish the different interactions.

Physisorption: The three kinds of forces that are responsible for physisorption are attractive dispersion forces, short range repulsive forces, and forces due to permanent dipoles within the adsorbed molecules.\(^2\) The binding energy of these forces is weak as characterized by the heats of adsorption and are on the order of 0.1 to 2.0 eV.\(^2\) Because of the weak bonding energy involved, physisorption is not considered to be a dominant mechanism inside the thruster.\(^2\) Where the component temperatures are about 1500°C. However, because a molecule can jump from site to site many times before desorption, physisorption may play an important role in the kinetics of dissociative chemisorption as a precursor state.\(^21,23\)

Chemisorption: Chemisorption is defined as the adsorption of atoms or molecules involving electron transfer or sharing with surface atoms. Generally, there are three types of chemisorption processes identified: molecular, dissociative, and sorption layer formation.\(^21\) Molecular chemisorption is characterized by heats of adsorption about 6-5 eV.\(^21\) In dissociative chemisorption, heats of adsorption may be as high as 8 eV.\(^20\) Chemisorption is usually limited to a coverage of one monolayer or less. With some very reactive systems, such as 

\[ \text{Ta-O}_2, \text{ and Mo}-\text{O}_2, \text{ much more than a monolayer can be adsorbed and this is referred to as sorption layer formation.} \]

Because of the relatively high temperatures inside a thruster, dissociative chemisorption is believed to be the dominant mechanism. Reference 24 demonstrated chemisorption of N\(_2\) on molybdenum at temperatures up to 900°C. Studies have shown that nitrogen chemisorbed on tantalum is limited to about one monolayer,\(^21,26,27\) a fact of importance in the sputtering model to be discussed.

Chemisorption phenomena are highly specific to the surface material into the gas involved. For example, according to Refs. 21, 26, and 27, nitrogen will be chemisorbed by U, Ta, N\(_2\), Ti, Sr, Ni, V, and Nb. However, in the sputtering or deposition rate of Mo,\(^23\) Ta,\(^21\) Ti,\(^21\) W,\(^16\) and Nb,\(^16\) chemisorption has been found in the presence of nitrogen. There appear to be some ambiguities about the class of elements which apparently do not chemisorb nitrogen, but may form nitrides.\(^28\) These include Al, Si, Ni, and Fe. Changes of deposition rates have been reported by Ref. 27 with Al and Fe in nitrogen atmospheres.

Elements such as A\(_1\), and Fe do not chemisorb nitrogen or form nitrides.\(^21,27\) However no sputtering data exists in the literature for these systems.

Model of Surface Coefficient for Chemisorption

The chemisorption process, in many cases, can be described by a simple model of sticking coefficient behavior as a function of coverage. If \(a\) represents the probability that two identical sites are empty, and \(s\) is the sticking coefficient, \(a\), is given by \(23\).
\[
\sigma = \sigma_0 e^{-\frac{1}{\theta} \left[ 2(1 - \theta) \frac{(1 - (1 - \theta)B)}{(1 - (1 - \theta)B^2 + 1)} \right]}
\]

where

\[
\begin{align*}
B &= \frac{\omega}{kT_0} \\
\theta &= \text{fraction of surface covered with adsorbed species} \\
T_0 &= \text{surface temperature} \\
\omega &= \text{pairwise interaction energy} \\
\sigma_0 &= \text{stickling coefficient} \\
k &= \text{Boltzmann constant}
\end{align*}
\]

The pairwise interaction energy, \(\omega\), is negative for repulsive and positive for attractive interactions. For repulsive forces \(B\) possesses two limits of zero at \(\omega T_0 = 0\) and one at \(\omega T_0 = \infty\). For large attractive forces \(\omega^+\) \(B\) becomes \(-\infty\). \(B\) may be taken as the measure of the degree of short range order in the chemisorbed layer.

For purposes of the paper it is sufficient to look at only the limiting cases of Eq. (1). For large repulsive interactions energies with \(B = 1\) we have

\[
\begin{align*}
\sigma &= \sigma_0 (1 - \theta)^2 \\
&= \sigma_0 (1 - \theta) \\
&= 0
\end{align*}
\]

If there is no short range order in the chemisorbed layer and \(B = 0\) then

\[
\sigma = \sigma_0 (1 - \theta) \quad \text{for } \theta \leq 0.5
\]

which is the expression for dissociative adsorption. For the large attractive nearest neighbor interaction, Eq. (1) becomes

\[
\sigma = \sigma_0 (1 - \theta) \quad \text{for } \theta > 0.5
\]

which is usually referred to as the Langmuir isotherm.

Equations (2) to (4) are plotted in Fig. 5. Also shown are measured relative sticking coefficients of nitrogen or both molybdenum and (110) crystals. The experimental sticking coefficient data appear to follow the \((1 - \theta)^2\) relationship more closely than the form given in Eqs. (2) or (4). Because the exact sticking coefficients are not available for partially ionized and dissociated nitrogen, the general relationship of Eq. (1) cannot be used for this study. Eqs. (3) and (4) will be based for the sticking coefficient functions, because \(\sigma_0 (1 - \theta)^2\) best approximates the dissociative chemisorption data and \(\sigma_0 (1 - \theta)\) probably best represents the large repulsive sticking coefficient value due to the dissociated and ionized nitrogen inside the thruster.

In order that more than one monolayer be allowed to be chemisorbed, Ref. 7 includes an effective sticking coefficient \(\sigma_{\text{eff}} = \sigma_0 N/(N_0)\), where \(N_0\) is the adsorbed vapor pressure, and \(N\) is related to the number of chemisorbed layers. Because the Mo-N\(_2\) system appears to form only about one monolayer this factor will not be included in this study.

**Sputtering Model**

Several mechanisms have been suggested in the literature to account for the decrease of sputtering rates of metals in the presence of reactive gases. One mechanism is that for certain metal-gas systems an insulating layer is formed at the target allowing a surface charge to build up which retards the incident ions. Thus, the energy of the ions and the observed sputtering rate would be reduced. Most other studies do not consider this effect and conclude that the incident ion energy is unchanged and the actual sputter yield of the chemisorbed surface layer formed is reduced. This is the mechanism assumed for the model described herein.

Following Hrbáček, it is assumed that the sputtered flux of the metal surface \(F_0\), is a linear combination of the sputtered fluxes at full coverage \(F_{\text{full}}\) and that of a clean metal surface \(F_0 = 0\). In that case

\[
F_0 = F_{\text{full}}(1 - \theta) + F_{0,0} \quad \text{for } \theta = 0
\]

\[
F_0 = F_{\text{full}}(1 - \theta) + F_{0,0} \quad \text{for } \theta > 0.5
\]

\[
F_0 = F_{\text{full}}(1 - \theta) + F_{0,0} \quad \text{for } \theta < 0.5
\]

where \(\theta\) is the fraction of surface covered with adsorbed species. The experimental sputtering data of Figs. 2 and 3, because the spectral intensity is assumed to be directly proportional to the sputtered molybdenum flux.

The equilibrium chemisorption-sputtering process can be described by a simple rate equation

\[
\dot{\omega}(P)_{\text{atom}} = F_A, \quad \text{cm}^2 \text{sec}^{-1}
\]

where

\[
\begin{align*}
\dot{Z}(P)_{\text{atom}} &= \text{arriving flux of reactive gas atoms} \\
\dot{F}_A &= \text{removal flux of adsorbed gas atoms}
\end{align*}
\]

The species of particles removed during the sputtering process in the presence of a reactive gas may be either in the atomic, molecular, or ionic state. Usually, the fraction of molecular and ionic species is considered to be small. Hence, the \(1 - \theta)_{\text{chem}}\) value of the coverage is used in the rate equation for the removal flux. Equation (2) was chosen which describes atomic removal mechanism. If molecular removal were to be considered, \(F_A\) would have to be used in Eq. (6).

The ratio of sputtering at a given level of adsorption to that of a clean metal surface was defined as \(F/F_0\), which can be calculated by eliminating \(\theta\) from Eqs. (5) and (6) and choosing one of the sticking coefficient functions.

**Selection of \(\sigma = \sigma_0 (1 - \theta)^2\)** results in

\[
\frac{F}{F_0} = 1 - \frac{\sigma_0 \sigma(\theta)}{\sigma_0} + F_A \left( 1 - \frac{F_0}{F_0} \right)
\]

The choice of \(\sigma = \sigma_0 (1 - \theta)^2\) results in
\[
\frac{F_0}{F_{\text{d}}} = \frac{(2m_2(P) - F_A) + \sqrt{(F_A - 2m_2(P))^2 + 4\sigma_2(P)(F_A - \sigma_2(P))}}{2\sigma_2(P)}
\]  

where

\[m = \frac{F_0}{F_{\text{d}}}
\]

A discussion will follow concerning the assumptions in evaluating each parameter in Eqs. (7) and (8).

**Adsorption Rate**

\(Z(P)\) represents the total flux of reactive gas particles arriving at the target surface. This flux can be evaluated by kinetic theory with the assumption that in equilibrium the number of reactive particles entering and leaving the thruster are equal. This implies that there is no steady state gathering of reactive gases inside the discharge chamber.

The flux of molecules of reactive gas arriving at the screen grid surface is

\[Z(P)_{\text{mol}} = \frac{3 \times 10^{22} P}{v_{\text{mol}}}, \text{ cm}^{-2} \text{ sec}^{-1}
\]

where

\[P \quad \text{partial pressure of reactive gas, torr}
\]

\[M \quad \text{molecular weight of the reactive gas, amu}
\]

\[T_w \quad \text{temperature of reactive gas taken to be equal to the facility wall temperature, K}
\]

The flux of atoms sputtered on the target surface is equal to \(2Z(P)_{\text{mol}}\). Because nitrogen is chemisorbed dissociatively, \(Z(P)_{\text{ion}}\) is used in Eq. (9). \(P\) was obtained from the total gas pressure inside the vacuum chamber. The nitrogen atom flux incident on the screen grid consists of a variety of species including \(N_2, N_2^+, N, \) and \(N^+\). It is of interest to know the fraction of each species inside the thruster because the sticking coefficient of each species may be different. Estimates using the model of Refs. 30 and 31, indicate that only about 2 percent of the nitrogen is dissociated inside the thruster. The sticking coefficient, \(a_s\), of \(N^+\) and \(N^+\) on molybdenum is the thruster experimental conditions have been measured to be between 0.75 and 1.0 (Ref. 12).

Values found in the literature of the sticking coefficient, \(a_s\), for molecular nitrogen on clean molybdenum vary from 0.02 to 0.9 (Refs. 12, 13, 32). One of the reasons for the large variation in values of the sticking coefficient is that the studies have included many different kinds of surfaces such as foils, thin films, and single crystals. All of the calculations made here assume only dissociative nitrogen chemisorption and a value of 0.75 was chosen as a representative sticking coefficient for clean molybdenum for this study (Ref. 13). The other values of parameters used for the evaluation of Eq. (7) and (8) were \(T_w = 1000\) K and \(M = 28\).

In this study, it is assumed that no mercury is adsorbed on the molybdenum surface. This assumption is supported by the results of Refs. 19 and 40 which show zero coverage at 273°C to 293°C.

On the other hand, Ref. 41 indicates two desorption peaks at 100°C to 230°C and 440°C to 520°C. This implies that some mercury coverage is still possible at the steady state screen grid temperature of 350°C.

**Total Removal Rate**

The removal rate, \(F_A\), could include evaporation and sputtering. Desorption spectra of chemisorbed nitrogen on molybdenum indicate that evaporation commences at about 300°C. Reference 41 finds that \(H_2\) desorbs formed by sputtering molybdenum in the presence of nitrogen are stable at 400°C and 10^(-6) torr. Because the screen grid temperature of a thruster is less than that temperature, it was assumed that sputtering is the only significant removal mechanism of the adsorbed gas. Therefore, the sputtered flux, \(F_A\), may be written as

\[F_A = \frac{J_{N^+}}{e} \left[ 4S_{N^+} + J_{N^+} + 4S_{N^+} - 2S_{N^+} \right]
\]

where

\[J_{N^+} \quad \text{total nitrogen ion current density, A cm}^{-2}
\]

\[J_{N^+} \quad \text{doubly ionized current density, A cm}^{-2}
\]

\[S_{N^+} \quad \text{sputter yield of adsorbed nitrogen by singly charged ions}
\]

\[S_{N^+} \quad \text{sputter yield of adsorbed nitrogen by doubly charged ions}
\]

\[e \quad \text{elementary charge per ion}
\]

It is usually assumed that \(S_{N^+} = S_{N^+} 0.5 S_{N^+}\), where \(E\) is the ion energy. The average value of \(J_{N^+}\) was determined to be \(3.5 \times 10^{-3} \text{ A cm}^{-2}\) from the measured saturated ion current to the screen grid at a beam current of 2 A.

The current density profile of a 30-cm thruster is not uniform. It is likely that the optical spectrometer will indicate molybdenum intensities representative of average values rather than peak values. Therefore, an average current density \(J_{N^+} 0.5 E\) for the calculation of the removal rate was obtained when the data of Ref. 42 was extrapolated to a discharge voltage of 50 volts.

It is believed that the parameter \(S_{N^+}\) contains the greatest uncertainty of the calculations. There has been a very little experimental work done in measuring the sputtering yield of adsorbed gases. Reference 43 measured yields of nitrogen chemisorbed on tantalum by various inert gas ions. Reference 44 has measured sputtering cross sections. Sputtering yield x number of atoms in a monolayer coverage of sulfur chemisorbed on nickel as sputtered by inert gas ions. Sputtering data is compared to theoretical models and agreement is claimed by both authors. Best agreement between theory and data appears in Ref. 44 for the beam inert gas such as xenon and krypton. The values of \(S_{N^+}\) used for this study were calculated using the theory of Ref. 44. The model and calculations are presented in the appendix.
sidered, as shown in Fig. 6, are: (1) direct knock-off by the collision of the incident ion and adsorbed atom, (II) removal of adsorbed atom due to reflected incident ion, and (III) sputtering of adsorbed atom due to collision of adsorbed atom with the sputtered target atom. It is found that at low ion energies, direct knock-off by incident ions of adsorbed atoms (mechanism I) represents from half to all of the total sputter yield (Ref. 33 and appendix). Mechanism II contributions are uncertain due to the uncertainty in the value of the reflection coefficient, \( R_{12} \), to be used for Mo-N\(_2\) systems. Two values of \( R_{12} \) were chosen to bound the values of the sputter yield calculated for mechanism II. Values of sputter yield, calculated for mechanism III, were found to be negligible for the ion energies of interest herein. Values of sputter yields calculated for each mechanism are presented in the appendix.

Values of \( S_{g+} \) and \( S_{g++} \) were chosen from the curves of the sputter yield of adsorbed nitrogen (Fig. A-1) as a function of ion energy for each value of \( R_{12} \) used. An ion energy of 50 eV was selected to correspond to the thruster discharge voltage of 50 volts. The removal fluxes, corresponding to these sputter yields, calculated from Eq. (10) are 5.22×10\(^{15}\) atoms/cm\(^2\) sec (for \( R_{12} = 0.5 \)) and 2.39×10\(^{15}\) atoms/cm\(^2\) sec (for \( R_{12} = 0 \)). Winters and Sigmund state that the lower value of \( R_{12} \) is probably more realistic.

### Magnitude of the Effect

The ratio of the polyethylene sputtering rates of the completely covered surface, \( F_{0-0} \), and the clean surface, \( F_{0-0} \), was obtained from the low and high pressure plateaus of Fig. 3 for a discharge voltage of 50 volts and zero bias. A value of 0.1 was obtained. Figure 2 also indicates that a ratio of the magnitudes of the sputtering rates calculated for clean surface and the completely covered surface, according to these sputter yields, calculated from Eq. (10) is 5.22×10\(^{15}\) atoms/cm\(^2\) sec (for \( R_{12} = 0.5 \)) and 2.39×10\(^{15}\) atoms/cm\(^2\) sec (for \( R_{12} = 0 \)). Winters and Sigmund state that the lower value of \( R_{12} \) is probably more realistic.

### Comparison of Experimental with Sputtering Model

Figure 7 shows the comparison of the experimental data of the zero bias curve of Fig. 3 with the sputtering model (Eq. (7)). The two curves using \( F_{A} = 5.22 \times 10^{15} \) and \( 2.39 \times 10^{15} \) atoms/cm\(^2\) sec represent the two limiting values used for the sputtering yield of the adsorbed gas. It is evident that the choice of the lower value of \( R_{12} \) which assumed an ion reflection coefficient of zero is in good agreement with the experimental data. This result indicates that the direct collision (mechanism I) is probably the dominant sputtering process. It should be noted that the ratio of limiting values \( F_{A}/F_{0-0} \) in Eq. (7) was obtained from the experimental data of Fig. 3.

The removal rate, \( F_{A} \), can be also calculated from Eqs. (4) and (6) with \( \theta = 1/2 \) as

\[
F_{A} = S_{0}^{2}(P_{0-0}^{1/2})
\]

from which an effective sputtering yield \( S_{g,eff} \) can be obtained from the following equation,

\[
S_{g,eff} = \frac{Z(P_{0-0})^{1/2}}{e^{2} \sigma r_{1/2}^{2}}
\]

with \( Z(P_{0-0})^{1/2} \) evaluated at \( F_{A}^{1/2} \)

\( S_{g,eff} \) represents a sputter yield where the different charged ion species are averaged. Equation (11) results in a removal rate of 2.67×10\(^{15}\) atoms/cm\(^2\) sec. Use of Eq. (12) gives a value of \( S_{g,eff} \) equal to 0.126 atoms/ion. Table 1 presents the values of \( S_{g,eff} \) calculated for the other curves of Fig. 3. Comparison of these values with those presented in Table 1-1 for \( S_{g} \) (with \( R_{12} = 0 \)) indicates that \( S_{g} \) is in good agreement with \( S_{g,eff} \) at a given ion energy. This occurs because the ratio of \( S_{g} \) to \( S_{g,eff} \) from Eq. (10) is small and \( S_{g} \) does not increase rapidly with ion energy.

As previously discussed, various models of the sticking coefficient can be used. The two functions chosen were \( s = s_{0}(1 - \theta) \) and \( s = s_{0}(1 - \theta)^{2} \). Figure 8 shows the comparison of the two sticking coefficient models using \( F_{A} = 2.67 \times 10^{15} \) atoms/cm\(^2\) sec. It was noted before that for dissociative nitrogen adsorption the \( s = s_{0}(1 - \theta)^{2} \) equation approximated some data found in literature. In Fig. 8 it appears that to fit the experimental data of this study \( s = s_{0}(1 - \theta) \) is a better approximation. This may be due to the small but very reactive fraction of nitrogen atoms and ions present in the thruster discharge chamber.

### Discussion of Criteria for Predicting the Onset of Environmental Effects

Several criteria have been developed in the past for evaluating conditions for clean surface sputtering. A brief discussion will follow on each of these.

**Flux ratio**. Yonta and Harrison\(^{46} \) derived one of the earliest criteria in 1960. It requires that the ion beam density incident on the target should be much greater than the particle density of the background gases. At 1×10\(^{-6}\) torr, where an effect in the thruster is observed, the ratio for our experimental conditions becomes

\[
\frac{J_{Hg,T}}{Z(P_{0-0}^{1/2})} = \frac{2.12 \times 10^{16}}{5.1 \times 10^{14}} \text{ cm}^{2} \text{ s}^{-1} \text{ mol}^{-1} \text{ s}^{-1} \]

Therefore, the mercury ion flux to the screen grid is found to be much greater than the molecular nitrogen flux. Thus, the criteria is found to be inadequate for the conditions of our study.

**Poisoning ratio**. The ability of the ions to sputter the adsorbed gas is the important criterion. Therefore, a "poisoning ratio" was defined in Ref. 47 as the ratio of the arrival flux of reactive gas to the removal flux of the target atoms (including the adsorbed gas). This ratio was used for Al-02 systems bombarded with high energy (2.5 to 10 keV).
ions where the sputter yields of the adsorbed gas and clean metal are probably comparable. As shown earlier, the large difference in sputter yields between the adsorbed gas (nitrogen) and the clean metal (molybdenum) at low ion energies lead to a modified “poisoning ratio,” equivalent to Eq. (6), which requires the use of the sputter yield of the adsorbed gas.

**Transition pressure.** Reference 11 defines a transition pressure, \( P_0 \) (torr), at which a chemical reaction takes place between the target surface and the chemisorbed gas.

\[
P_0 = \frac{3 \times 10^{-5} R}{SG}
\]

where

- \( R \) sputtering rate of the clean target, \( \text{A/min} \)
- \( P_0 \) partial pressure of reactive gas, torr
- \( SG \) Gibbs' free energy function for the reaction, kcal/mole

The author claims excellent agreement between his model and sputtering and thin film deposition measurements, but it will be shown, that this equation in its present form appears not to be valid at the ion energy range of our interest.

As shown in Figs. 2 and 3, the pressure range over which the effect takes place is quite large (2 orders of magnitude), therefore, the definition of \( P_0 \) is difficult to define. \( P_0 \) may be determined approximately from the data of Fig. 3 as the point where the tangent at the center of the curve (point of symmetry) deviates from the curve at the lower part of the curve. The transition pressure values of the four data curves from Fig. 3 are listed in Table 1. These values of \( P_0 \), as predicted in Eq. (13) and are shown in Fig. 9. The calculated transition pressures were obtained using the appropriate sputter yields of molybdenum from Ref. 13. In order to compare the relative behavior of Eq. (13) with the results from the data of Fig. 3, the curve was normalized to a point where the discharge voltage was 50 volts and zero grid bias.

It is apparent that the calculated \( P_0 \), based on the metallic sputter yield predicts a much larger increase with ion energy than was obtained from Fig. 3. A much better agreement is found when the transition pressure is assumed to be proportional to the sputter yield of the adsorbed gas. The sputter yields, \( Y_{ads} \), were obtained using Eq. (12) and the data of Fig. 3 and are listed in Table 2. Equation (12) shows that for \( \gamma = 1/2 \) the shift with pressure of the data sets is proportional to the sputter yield of the gas \( Y_{gas} \).

The agreement claimed by Fig. 8, par. 2, due to the apparent invariance of \( Y_{ads} / Y_{gas} \), is not seen at any pressure, because at high ion energies where this invariance was made, the sputter yields of the adsorbed gas and the target clean surface may be about equal 11. At low ion energies, as found in our study, the sputter yields of the adsorbed gas and the target metal appear to be quite different. Our limited recent data consists of the sputter yield of the \( \gamma \) rather than the target should be used in calculating the transition pressure, \( P_0 \), from Eq. (13).

**Estimated Environmental Effect at Discharge Voltage of 32 V**

Normal operating conditions of a 30-cm diameter 98 ion thruster are a beam current equal to 2 A and a discharge voltage equal to 32 volts. At these conditions, as pointed out earlier, the sputtering rate is affected by the facility environment. The model that has been developed in this study offers a means of calculating the effect at a given facility pressure. Data in this study has been presented dealing only with nitrogen, therefore the extrapolation to discharge voltage of 32 volts can only strictly apply to nitrogen pressure in the facility. According to Ref. 19 all residual gases tested that are found in a typical vacuum facility show sputtering characteristics similar to that of nitrogen. However, in order that the effect of all residual gases be included in the model more sputtering data will be required along with a better understanding of how various gases are adsorbed and sputtered on a surface in the presence of each other. It should also be recalled that many assumptions were made in the model where accurate information was lacking in the literature such as the sticking coefficient function, the neglect of mercury adsorption on the target surface, neglect of other possible removal mechanisms, and finally the many assumptions that went into the calculation of the sputter yield of the adsorbed gas.

The estimated environmental effect of nitrogen, at a discharge voltage of 32 volts, is seen in Fig. 10. This curve is a plot of Eq. (8), using the sputter yield of nitrogen at 32 volts as obtained from the appendix. \( P_0/P_{00} \) was chosen to be the same as for discharge voltage of 50 volts. From Fig. 10, it is evident that at this low voltage, the curve for the sputter yield is much steeper than at the higher ion energies. Therefore, a small error in the ion energy will result in a rather large change in the calculated sputter yield which will lead to a corresponding error in Fig. 10.

The temperature of the screen grid is cooler at the normal operating conditions than those for the conditions of Fig. 3. This may result in an increase of mercury adsorption on the screen grid surface, thus complicating, the adsorption-sputtering process discussed in this study. Neglecting these possibilities, it is seen from Fig. 10 that operation of a thruster in nitrogen atmosphere at 1x10^-7 torr, results in a sputtering rate of the molybdenum screen grid which is only about 12 percent less than that of clean surface conditions.

**Conclusions**

In the past, sputtering rates of ion thruster components have been observed to decrease substantially in the background gas pressure in the test facility was increased. Relative sputtering rates of the screen grid have been determined by spectral intensity as functions of various thruster parameters in the presence of one of the reactive gases, such as nitrogen. The facility was operated in a vacuum chamber. In this paper, surface interactions are discussed that are thought to be possible for the environmental effect. Adsorption was found to be the mechanism that most likely leads to a reduction of the sputter yield of a surface in the presence of a reactive gas. A model was presented.
which appeared to be in general agreement with the experimental results. It assumes that sputtering is the only removal mechanism of the chemisorbed gas. The sputtering yield of the adsorbed gas is shown to be a determining factor of the sputtering rate of a metal target in the presence of a reactive gas. A sputtering yield of the adsorbed gas was calculated using the theoretical model of Winters and Sigmund. It was found that at the low ion energies existing in an ion thruster, sputter yields of adsorbed gases are substantially higher than the sputter yields of metals considered.

It was found that models are available which show promise in determining the onset of an environmental effect. However, determining the magnitude of the effect, at least at low ion energies, one must still rely upon experimental methods.

An attempt was made to predict the magnitude of the environmental effect at normal operating thruster conditions of 32 volts and 2 A beam. At these conditions it is impossible to measure the effect experimentally due to large vacuum facility limitations. It is concluded that the effect is not large at \( 1 \times 10^{-7} \text{ Torr} \) of nitrogen pressure. However, it is felt that more data is required in order that models presented in this study may be applied to general thruster test facility conditions.

**Appendix - Theoretical Model of Sputter Yields of Chemisorbed Gases**

The model of Winters and Sigmund assumes the sputtering process of chemisorbed gases on a metal surface to be due to a series of binary elastic collisions involving the bounding ions, the metal target, and the adsorbed gas. With similar arguments, Sigmund has been able to calculate, with reasonable accuracy, the sputter yields of "clean" materials at intermediate and high energies.

The sputtering process is postulated to be composed of three mechanisms, as illustrated in Fig. 6, which include:

1. An incident ion collides directly with an adsorbed nitrogen atom, which is then reflected from the target lattice. The scattering process is approximated by Thomas-Fermi power cross section with a Born-Mayer zero power interaction chosen for low energy ions. The contribution to the sputter yield of atomic nitrogen due to this mechanism is obtained by combining Eqs. (6) and (5) of Ref. 33 (assuming a zero power interaction) to yield

\[
S_1 = \frac{n_3 C_1}{a} \cos (\ln x) \quad (A1)
\]

where

- \( n_3 \) number of atoms contained in a saturated monolayer
- \( a \) screening radius equal to 0.219 Å
- \( C_1 \) constant equal to 24 Å
- \( \lambda_0 \) incident ion energy, eV
- \( E \) binding energy of the adsorbed atom, eV
- \( M \) molecular weight

\( \theta \) angle of incidence of the ion

\( C_0 \) constant

(Particle subscripts are defined in Fig. 6.) Sigmund states that the screening radius or the constant \( \lambda_0 \) may be off as much as a factor of 2.45

(II) The incident ion penetrates into the target and is eventually reflected. On its way out it knocks off an adsorbed atom. The ratio of this sputtering yield, \( S_{II} \), to that of \( S_1 \) is derived to be:

\[
S_{II} = R_{12} \left[ 4 - \frac{4 \log x}{3 \left( 1/3 - 1 \right)} \right] \cos \theta \quad (A2)
\]

where \( R_{12} \) is an experimentally measured ion reflection coefficient dependent on the angle of incidence and ion energy. This calculation assumes a power interaction of \( m = 1/3 \), but according to Winters and Sigmund it is sufficiently accurate for a qualitative estimate to be compared to \( m = 0 \) interactions.

(III) The incident ion sputters a target atom, when the ion is ejected it knocks off an adsorbed ion. The contribution from this process is calculated by:

\[
S_{III} = 4 \gamma_2 \gamma_3 \left( 1 - \frac{\left( 1 + \log y \right)}{y} \right) \quad (A3)
\]

where

- \( \gamma = \gamma_1 \gamma_2 \gamma_3 \)
- \( C_{23} \geq C_0 \)
- \( U_2 \) sublimation energy of the target
- \( S_{12} \) sputtering rate of clean target at ion energy \( E \)

Assuming that the sputtering processes are additive, the total sputtering yield becomes

\[
S_G = S_1 + S_{II} + S_{III} \quad (A4)
\]

**Discussion of Model**

Table A-1 shows the calculated sputtering yields for each of the three mechanisms described above for nitrogen chemisorbed on molybdenum and bombarded by mercury ions. In making these calculations several assumptions were made, which will now be discussed.

The constant, \( n_{1+} \), in Eq. (A1) was taken to be \( 1 \times 10^{15} \) atoms/cm\(^2\). This number represents a monolayer coverage in which approximately each surface target atom has one chemisorbed nitrogen atom attached to it. Under normal molecular dissociative adsorption conditions, it is then a complete monolayer of nitrogen on molybdenum is possible under conditions such as existing on a mercury thruster, the presence of molecular or atomic nitrogen, adsorption sites may be filled which normally are not.

Difficulty arises in choosing the proper value of the binding energy, \( U_3 \), because of the lack of available data in the literature. Winters and Sigmund approximate the binding energy for atoms as one-half the sum of the dissociation energy and the heat of adsorption. For a W-N\(_2\) system they estimated this value to be 6.7 eV. For lack of a
better number, the same value will be used here for Hg-Hg system.

The ion reflection coefficient, $R_{12}$, represents a parameter which is also not readily available in the literature. There even appears to be some ambiguity in defining the reflection coefficient. For most gas ions incident on a clean tungsten surface the reflection coefficient of $10^{-6}$ to $10^{-2}$ have been measured for ion energies between 100 and 1000 volts. Values between 0.1 and 0.4 (increasing with decreasing ion energy) have been measured for alkaline metal ions on a molybdenum surface. It has been observed that $R_{12}$ appears to increase with increasing impurity levels on a target surface. Winters and Sigmund believe that $S_{11}$ was overestimated by their choice of $R_{12}$ equal to 0.6. Therefore, following their example, two values of $S_{0}$ are presented in Table I, one of which assumes $R_{12}$ equal to 0.5 and the other equal to zero.

It is evident from Table A-I that contributions to $S_{0}$ from $S_{1}$ and $S_{2}$ (when $R_{12} = 0.5$) dominate much larger than 100 volts does $S_{11}$ contribute significantly to the total sputtering yield $S_{0}$.  

Figure A-I summarizes the various sputtering yields of nitrogen on molybdenum for a mercury ion energy. Shown are the two calculated curves of $S_{0}$ using the two limiting values of the reflection coefficient. For comparison the sputtering yields of nitrogen chemisorbed on tungsten, as sputtered by xenon ions, as well as the sputtering yield of "clean" molybdenum by Hg ions are also shown. As pointed out in the main text of this report, best agreement between theory and thruster experiments was found when the $S_{0}$ values with $R_{12} = 0$ was used. Similar results were found by Winters and Sigmund. Steep decrease in $S_{0}$ for ion energies less than 40 eV remains to be verified experimentally.

References


41. Reynolds, T. W., Unpublished data.


TABLE 1. - EFFECTIVE SPUTTERING YIELD OF ADSORBED NITROGEN AS CALCULATED FROM EQ. (12) AND TRANSITION PRESSURE AS OBTAINED FROM FIG. 3

<table>
<thead>
<tr>
<th>Ion energy (discharge voltage + bias), V</th>
<th>Transition pressure, P0, torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.26 x 10⁻¹</td>
</tr>
<tr>
<td>60</td>
<td>1.73 x 10⁻¹</td>
</tr>
<tr>
<td>70</td>
<td>2.10 x 10⁻¹</td>
</tr>
<tr>
<td>80</td>
<td>2.34 x 10⁻¹</td>
</tr>
<tr>
<td>70 1.26 x 10⁻¹</td>
<td>7 x 10⁻⁶</td>
</tr>
<tr>
<td>80 2.10 x 10⁻¹</td>
<td>9 x 10⁻⁶</td>
</tr>
<tr>
<td>80 2.34 x 10⁻¹</td>
<td>1 x 10⁻⁵</td>
</tr>
</tbody>
</table>

TABLE A1. - CONTRIBUTIONS OF VARIOUS SPUTTERING MECHANISMS OF CHEMISORBED NITROGEN ON MOLYBDENUM EMBARDED WITH MERCURY IONS

\[ \left( n_3 = 1 x 10^{15}, U_3 = 6.7 \text{ eV}, C_0 = 1.8 \times 10^{-16} \right) \]

<table>
<thead>
<tr>
<th>Ion energy, eV</th>
<th>( S_1 ) ( R_{12} = 0 )</th>
<th>( S_{II} ) ( R_{12} = 0 )</th>
<th>( S_{III} ) ( R_{12} = 0 )</th>
<th>( S_G = S_1 + S_{II} + S_{III} ) ( R_{12} = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.6 x 10⁻²</td>
<td>0</td>
<td>1.62 x 10⁻²</td>
<td>1.5 x 10⁻²</td>
</tr>
<tr>
<td>40</td>
<td>6.78 x 10⁻²</td>
<td>0</td>
<td>8.03 x 10⁻²</td>
<td>6.78 x 10⁻²</td>
</tr>
<tr>
<td>60</td>
<td>1.41 x 10⁻¹</td>
<td>0</td>
<td>1.75 x 10⁻¹</td>
<td>1.41 x 10⁻¹</td>
</tr>
<tr>
<td>80</td>
<td>1.93 x 10⁻¹</td>
<td>0</td>
<td>2.46 x 10⁻¹</td>
<td>1.93 x 10⁻¹</td>
</tr>
<tr>
<td>100</td>
<td>2.33 x 10⁻¹</td>
<td>0</td>
<td>3.04 x 10⁻¹</td>
<td>2.36 x 10⁻¹</td>
</tr>
</tbody>
</table>
Figure 1. - Screen grid erosion rate as a function of facility pressure. Beam current, 2 A (Fig. 14 of ref. 3).

Figure 2. - Mo I (3798.8 nm) line intensity as a function of facility pressure with nitrogen added. Beam current, 2 A.
Figure 3. - MoI (3798.8 nm) line intensity as a function of facility pressure with nitrogen added. Beam current, 2 A, discharge voltage, 50 V.

Figure 4. - Comparison of various sputtering and deposition rates in the presence of oxygen.
Figure 5 - Comparison of sticking coefficient functions
Figure 6. - Postulated sputtering mechanisms of adsorbed gas (ref. 33).

Figure 7 - Comparison between sputtering data and model (eq (7)) for limiting values of $s_G$, as a function of facility pressure.
Figure 8. - Comparison between sputtering data (fig. 3) and eqs. (7) and (8) as a function of facility pressure with nitrogen added. Discharge voltage, 50 V, 0 bias, beam current, 2 A.
Figure 9 - Comparison between measured and calculated (eq. (13)) transition pressure as a function of effective ion energy.
Figure 10. - Estimated sputtering rate (eq. (7)) as a function of facility pressure with nitrogen added at a voltage of 32 V and beam current of 2 A.
Figure A-1 - Comparison of calculated and measured sputtering yields as a function of ion energy.
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