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Sputtering Threshold Energies of Heavy Ions

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Sputter erosion in ion thrusters has been measured in lifetests at discharge voltages as low as 25 V. Thruster operation at this discharge voltage results in component erosion rates sufficiently low to satisfy most mission requirements. It has been recognized that most of the internal sputtering in ion thrusters is done by doubly charged ions. Knowledge of the sputtering threshold voltage of a xenon-molybdenum system would be beneficial in understanding the sputtering process as well as making more accurate calculations of the sputtering rates of ion thruster components. Sputtering threshold energies calculated from various formulations found in the literature result in values ranging from 28 to 200 eV. It is evident that some of these formulations cannot be relied upon to provide sputtering thresholds with any degree of accuracy. This paper re-examines the threshold energies measurements made in the early sixties by Askerov and Sena, and Stuart and Wehner. The threshold voltages as derived by Askerov and Sena have been reevaluated by using a different extrapolation method of sputter yields at low ion energies. The resulting threshold energies are in general similar to those measured by Stuart and Wehner. An empirical relationship is derived for mercury and xenon ions for the ratio of the sputtering threshold energy to the sublimation energy as a function of the ratio of target to ion atomic mass.

Nomenclature

E	ion energy, eV
E_s	sublimation energy of target, eV
E_{th}	sputtering threshold energy, eV
K	constant in Eq.3
M_1	atomic mass of incident ion
M_2	atomic mass of target
Y	sputter yield as defined by Eq. 3
β	energy transfer factor as defined by Eq. 1

Introduction

Sputtering, a process by which a target atom is removed by an impinging ion, has been studied in great detail since the early sixties[1]. Despite this, the need exists for accurate sputter yield information, experimental and analytic, at low ion energies and heavy ions[2]. Near threshold, sputtering is of importance, for example, in impurity release in Tokamak fusion devices[3] and ion thrusters for space propulsion[4]. Most work to date has been performed to examine the sputtering of low energy, light ions. These data are valuable for certain fusion processes. Heavy ion sputtering is of importance in xenon ion thruster operation. In these devices, erosion of the thruster's molybdenum ion extraction grids must be minimized to assure appropriate mission lifetime. At higher power densities, it has been found that the thruster discharge voltage, which determines the impinging ion's energy must be kept below 28 V to ensure low wear-rates of the upstream surface of the positive grid[5]. It has been recognized that most of the internal sputtering in ion thrusters is due to doubly charged ions which have energies twice that of singly charged ions. Knowledge of the sputtering threshold energy of the Xe^+-Mo system would increase the understanding of the sputtering process as well as make it possible to calculate the sputtering rates more accurately in an ion thruster.

Threshold energy is defined as the ion energy at which the sputtering yield effectively is reduced to zero. Stuart and Wehner[6],in the early sixties, attempted to quantify the threshold energies from their low energy sputtering studies. They concluded that sputtering threshold voltages were independent of the ion mass and proposed that the threshold voltage was approximately equal to four times the sublimation energy of the target material. In a later study Hotston derived the following relationship which included the ion mass:

$$E_{th}/E_s=1/\beta=(M_1+M_2)^2/4M_1M_2 \qquad (1)$$

Further studies revealed sputtering threshold energy values for light ion sputtering to be much higher than the relationship suggested by Stuart and Wehner. Equation 1 has been recognized as the lower limit of the threshold energy[2,7]. Numerous other attempts have been made to formulate the threshold energy either by analytical models or semi-empirical formulas. These analysis have considered collision cascades[1], few collisions[8], 3-body collisions[9], and many body collisions[2]. Most measurements of sputtering threshold energies have indicated values which are twice the sublimation energy of the target or higher. However, several studies have indicated values that fall below those of twice the sublimation energy [10,11].

Sputtering threshold energy formulas summarized by Eckstein et al.[2] indicate threshold energies of 28-200 eV for a Xe^+-Mo system. It is evident that these formulations, obtained by various analytical models and semi-empirical means, cannot be relied upon to determine sputtering thresholds with any degree of accuracy. Thus, Eckstein stressed the need for more reliable data with heavy ions.

The objective of this paper is to review the data obtained by Stuart and Wehner and Askerov and Sena[12] and show that this data with a new method of extrapolation of the Askerov and Sena sputtering yield data exhibit the expected periodicity with the sublimation energy as a function of atomic number. Wehner's sputtering data has come under some criticism because of possible target contamination due to inappropriately high pressure in his test apparatus leading to incorrect sputtering yields.[13] Askerov and Sena's work has mostly been ignored in sputtering literature. Further, a threshold energy is deduced from the data for a Xe^+- Mo system, and an empirical relationship is derived for the ratio of the sputtering threshold energy to the sublimation energy as function of the ratio of target to ion atomic mass.

Sputtering Threshold Energy and Heat of Sublimation

Sputtering theory indicates that both the sputtering yield and the sputtering threshold energy are proportional to what has been referred to as the binding energy. Most often, the binding energy is assumed to be equal to the sublimation energy of the target. [14] Because the sublimation energies and measured threshold energies exhibit similar periodicity with atomic number, the heat of sublimation characteristics will be discussed first. Figure 1 shows the sublimation energies[15] of target materials for which Stuart and Wehner and Askerov and Sena have measured the sputtering threshold energies. The three largest sets of data consist of transition metals, from the 4th, 5th and 6th periods of the periodic table. These groups of elements have filled 3d, 4d and 5d electronic shells, respectively. The sublimation energies are seen to increase linearly with decreasing atomic number for periods compromising metals in the 5th and 6th period, with the exception of zirconium and tantalum. These metals exhibit lower sublimation energies than the maximum values. There is considerable scatter in the data for elements in the 4th period.

Experimental data of the sputtering threshold energies from the published literature[6,12] are shown in Figures 2a and 2b. Figure 2a shows the threshold energy measurements of various metal targets with mercury ions as a function of the target atomic number. Figure 2b shows the Stuart and Wehner data for xenon ions. Askerov & Sena obtained the threshold voltages by extrapolating the sputtering yield measurements to zero by assuming a $(E-E_{th})^3$ relationship over a 50 to 250 eV range. Wilhelm, however, points out that the assumption of a cubic relationship is not justified theoretically. Therefore, the Askerov and Sena data were extrapolated for the study described herein using $(E-E_{th})^2$ relationship as derived by Wilhelm. The extrapolation to zero yield was performed using sputtering yield data at mercury ion energies less than 100 eV. The extrapolation of Askerov and Sena's data with the quadratic relationship increased those threshold energy values by an additional 1 to 15 eV. It is apparent from Figure 2a that there are considerable differences between Stuart and Wehner's and Askerov and Sena's modified data for some of the elements. The differences range from 1 eV for copper to as much as 11 eV for titanium and zirconium. Some of the differences may be explained by the significant uncertainty (scatter) of the Askerov and Sena's sputtering yield data.

The measured threshold energy characteristics as a function of atomic number in Figures 2a and 2b show a similar periodicity to the heat of sublimation energies as shown in Figure 1. The similarities are especially prominent in Stuart and Wehner's xenon data shown in Figure 2b. Lines connecting the threshold energy data in Figures 2a and 2b were generated similar to those of Figure 1 using the following sets of elements (Zr-Nb-Ag and Ta-W-Au) in the 5th and 6th period, respectively. The sputtering threshold data for target atomic masses from 40 to 80 amu follow about the same pattern as the heat of sublimation data.

The impact of target to ion mass ratio can be seen in Figure 3a, where the ratio of the sputtering threshold energy to the sublimation energy is plotted as a function of the mass ratio using the data shown in Figures 1, 2a and 2b. Also shown is the $1/\beta$ parameter as defined by Equation 1. The data in Figure 3a suggests that the sputtering threshold to the sublimation energy ratio varies approximately from 3 to 8. This indicates that Equation 1 predicts the ratios for mercury and xenon ions incident on metal targets are too low.

By selecting the threshold energy values from Figures 2a and 2b which fall close to the drawn lines, the ratio of the threshold to sublimation energy values narrow substantially as shown in Figure 3b. The ratio values of Figure 3b fall close to Wilhem's predicted range of 3 - 5. A curve-fit of these data using mercury and xenon ions yields the equation:

$$E_{th}/E_s = 4.4 - 1.3 \log(M_2/M_1) \qquad (2)$$

This relationship can be used to derive low energy sputtering threshold energies of selected materials. For example, for a Xe^+ - Mo system, the ratio of threshold to sublimation energy is 4.5 and the threshold energy is equal to 31 eV assuming a sublimation energy of 6.89 eV for molybdenum.

Sputtering Yields of Metals with Heavy Ions

The sputtering yield near threshold energies can be obtained by Wilhelm's relationship:

$$Y = K^* E_s\,(E/E_s - E_{th}/E_s)^2 \quad \text{(atoms/ion)} \qquad (3)$$

where the constant K is a function of ion-atom scattering cross-section, density of target atoms. The value of K can be estimated by normalizing Equation 3 by choosing the appropriate sputtering threshold energy and the available xenon ion sputtering yields[16] (100 eV) for each target. The values of K, threshold energies as determined from Equation 2 and the sputtering yield formula (Equation 3) for selected targets are shown in Table 1. For example, the sputtering yield formula for the Xe^+-Mo system is of greatest interest:

$$Y = 1.3 \times 10^{-5}\,(E-31)^2 \quad \text{(atoms/ion)} \qquad (4)$$

This equation can be used to calculate the internal sputtering rates in a xenon ion thruster and the results can be compared to measured erosion rates. However, the measured internal sputtering rates of thruster components such as a molybdenum grid in relatively short lifetests[17] have uncertainties of 50 to 100% thus making a comparison to calculated rates problematical. These measurements also have to take into account the effects of background gases if the criteria for a dynamically clean surface has not been satisfied in the lifetest[18]. The validation of this sputtering yield relationship for low energy ions awaits the results of extended wear tests of ion thrusters.[19]

Conclusions

Formulations for the sputtering threshold energy found in the literature have a wide disparity of values thus they can not be relied upon to provide the threshold energy with any degree of accuracy. For example, calculations from these formulations show sputtering threshold values between 28 - 200 eV for a Xe-Mo system. Also measured threshold voltages vary over a large range of values. Accurate values of threshold energies would increase the understanding of sputtering processes in an ion thruster and facilitate a more accurate calculation of sputtering rates in an ion thruster.

Sputtering threshold data of Stuart and Wehner, and Askerov and Sena from sixties (utilizing both xenon and mercury propellants) have been reexamined. Askerov and Sena data has been modified using a quadratic relationship to extrapolate to zero sputtering yields. The heat of sublimation has been used to estimate the binding energy defined in sputtering yield and sputtering threshold energy formulations. The close periodicity found between the heat of sublimation and the measured sputtering thresholds lends support to the credibility of the threshold data examined in this paper. Utilizing selected data which follow the periodicity with the sublimation energy, it was determined that mercury and xenon sputtering threshold energies were 4 to 5 times the respective sublimation energies. This result is consistent with Wilhelm's theory. It was determined that the sputtering threshold energy for a Xe^+-Mo system is approximately 31 eV. A sputtering yield relationship was derived using Wilhelm's formulation and the ratio of threshold energy to sublimation energy derived from a curve fit of selected data.

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Table 1. Selected target sputtering threshold energies for Xe ion impingement, K-values for Eq. 3, and sputtering yields (Eq.3) near threshold.

Element	Sputtering threshold energy, Eq.2, eV	Constant K for Eq.3.	Sputtering yield, Eq. 3, (atoms/ion)
Nb	34	4.6×10^{-6}	$4.6 \times 10^{-6} (E-34)^2$
Mo	31	1.3×10^{-5}	$1.3 \times 10^{-5} (E-31)^2$
Re	34	4.6×10^{-6}	$4.6 \times 10^{-6} (E-34)^2$
Ta	34	1.2×10^{-5}	$1.2 \times 10^{-5} (E-34)^2$
W	37	7.6×10^{-6}	$7.6 \times 10^{-6} (E-37)^2$
Zr	29	6.0×10^{-6}	$6.0 \times 10^{-6}(E-29)^2$

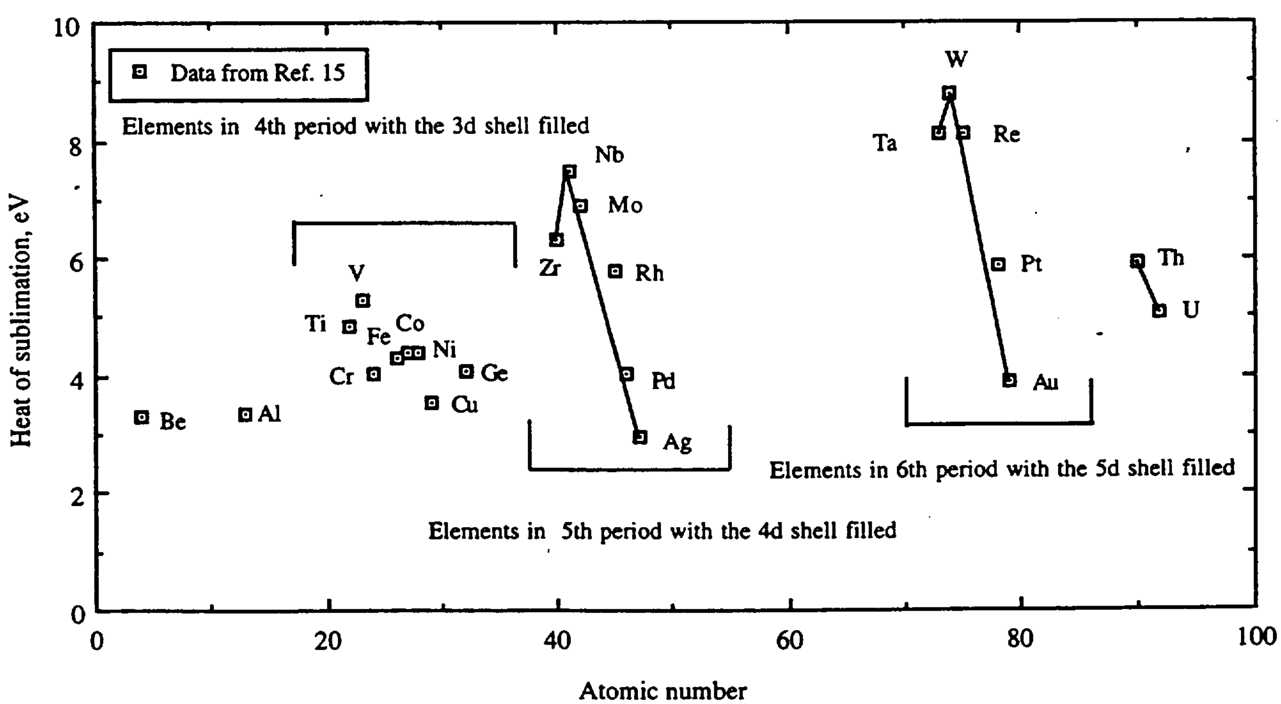

Figure 1. Heat of sublimation of target materials vs atomic number.

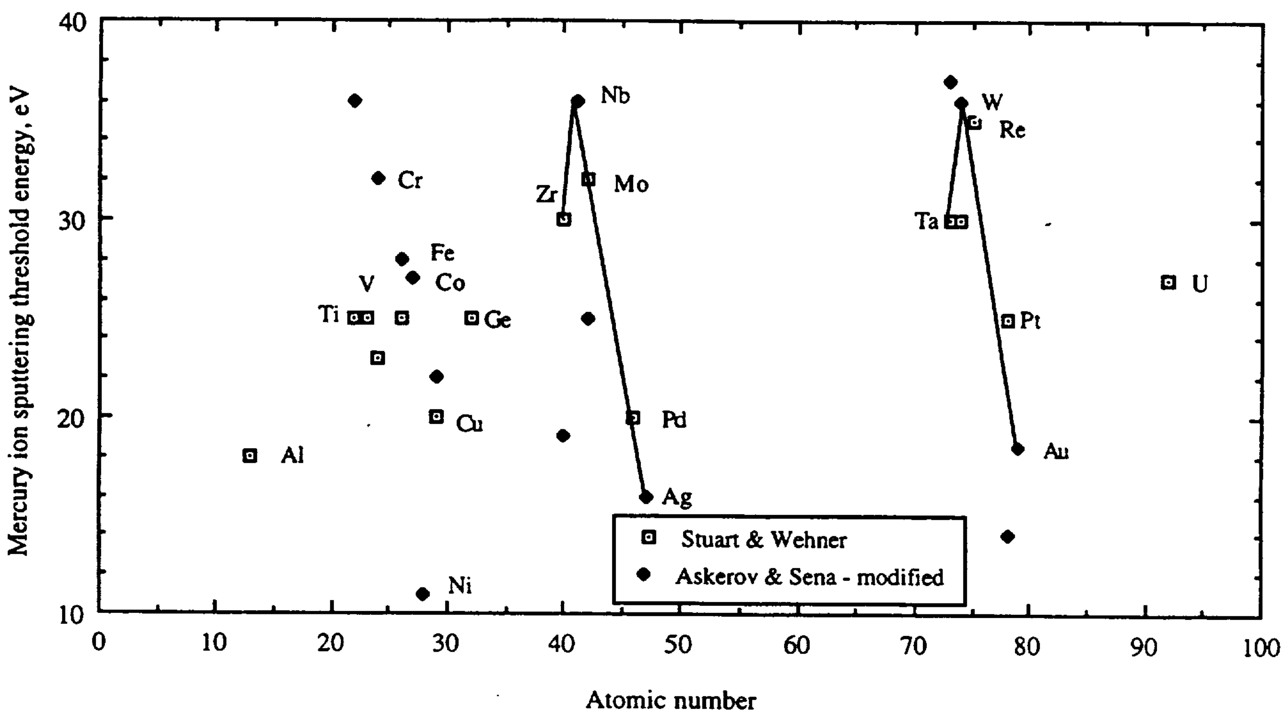

Figure 2a. Measured Hg threshold energies vs atomic number of target.

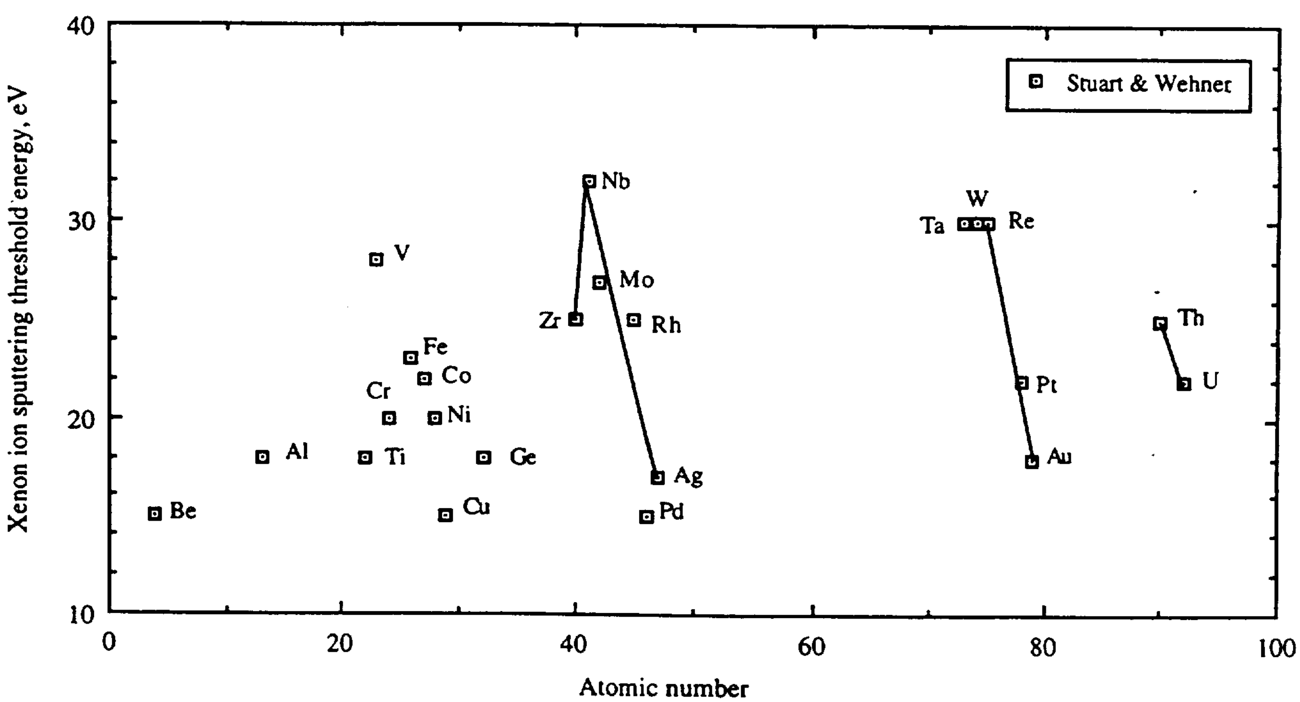

Figure 2b. Measured Xe threshold energies vs target atomic number.

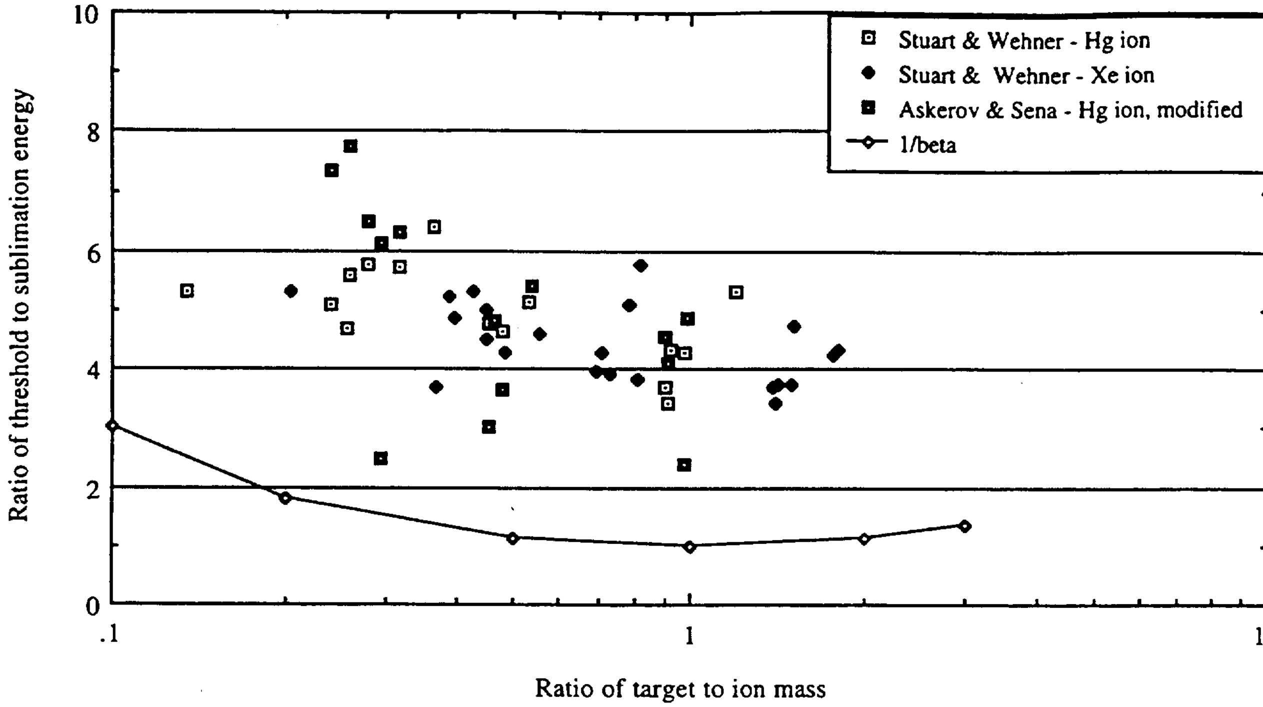

Figure 3a. Relative threshold energy vs ratio of target to ion mass.

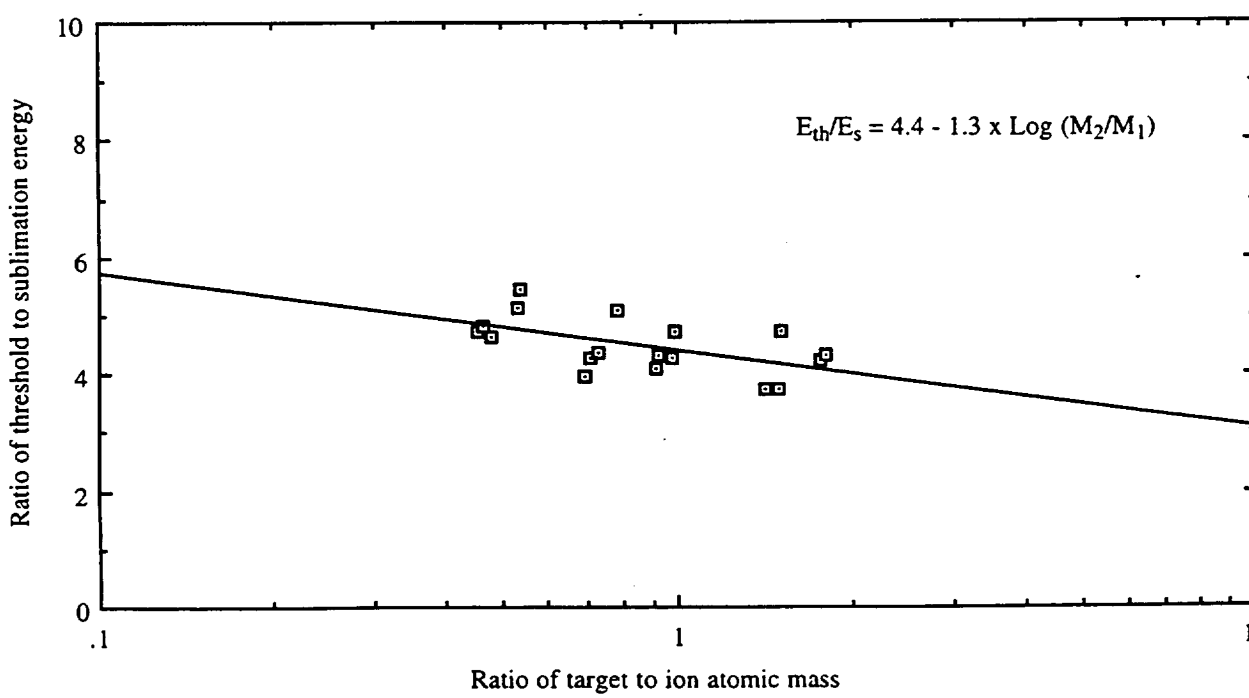

Figure 3b. Relative threshold energy vs ratio of target to ion mass for selected mercury and xenon ion-target systems.

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