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Monte Carlo Studies of Sputtering

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MONTE CARLO STUDIES OF SPUTTERING *

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ABSTRACT

A computer program has been developed to simulate the sputtering process using the Monte Carlo method and the binary collision approximation. This program is a result of the generalization of the TRIM computer program such that the target atom trajectories are followed in addition to those of the incident particles. This program, which includes electronic energy loss, uses an analytic formula which is based on realistic interatomic potentials for determining particle scattering angles and the energy transfer to target atoms. A model of the sputtering process has been developed for physically defining the surface and bulk binding energies necessary for calculations. A number of sputtering yield calculations have been performed for H, D, T, and 4 He ions incident on C, Ni, Mo, and Au targets for energies less than 10 keV. The validity of the Monte Carlo model is demonstrated by the good agreement between the calculated results and the most recent experiments.

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1. Introduction

Plasma contamination by sputtered wall material is one of the crucial problems for present plasma experiments and future fusion reactors [1]. The sputtering is caused primarily by low energy, light ions and neutrals from the plasma. Measurements of the small sputtering yields for light particles are inherently difficult, and sputtering theories [2, 3] are still not accurate enough to predict absolute values at low energies [4]. To provide some further insight into the sputtering mechanisms, a Monte Carlo method using the binary collision approximation has been applied to simulate the sputtering process.

Similar methods have been applied previously [5-8] to simulate sputtering, but the majority of the reported results [5-7] have been for heavier incident particles. Only the recently presented results of Maderlechner et al [8], using the MARLOWE [9] computer program, have dealt with light particle sputtering. Here we have used a generalization of the TRIM [10] computer program which treats particle transport in amorphous solids. This program, which includes electronic energy loss, uses an analytic formula [10, 11] which is based on realistic interatomic potentials for determining particle scattering angles and the concomitant energy transfer to target atoms. Thus, it is both fast, in terms of computer usage, and accurate within the constraints of the binary collision approximation.

A simplified model of the sputtering processes has been developed which is applicable to the Monte Carlo method. Parameters of this model are physically meaningful and are related to "surface" and "bulk" binding energies of the target atoms. A number of calculations have been performed for H, D, T, and ^4He ions incident on C, Ni, Mo, and Au targets for energies less than 10 kev. Comparisons are made between our computed results and those of the most recent experiments.

2. Monte Carlo Procedure and Sputtering Model

To simulate the sputtering process, the TRIM Monte Carlo computer program has been generalized to consider the trajectories of the target atoms as well as those of the incident ion. The full details of the TRIM computer program have been described elsewhere [10]. In brief, each particle starts with a given energy, position, and direction, and its trajectory is followed in a target, collision by collision, until its energy falls below a prespecified value or until it leaves the target surface. The particle changes direction as a result of binary nuclear (elastic) collisions and moves in a straight path between collisions. The particle's energy is reduced by nuclear and electronic (inelastic) energy losses, and these energy loss mechanisms are assumed to be independent. The target is assumed to be amorphous (atoms at random locations) so that the directional properties of a crystal lattice are ignored. The low energy, electronic energy loss ΔE_e is based on the velocity dependent treatment of Lindhard and Scharff [12]. Thus, $\Delta E_e = LNk \sqrt{E}$, where L is the pathlength between collisions, N is the target atomic density, k is a proportionality constant, and E is the particle's energy. For the results presented here, we have used the Lindhard and Scharff [12] expression for k and with $L = N^{-1/3}$. Although it is recognized that deviations from this electronic energy loss treatment are known to exist [10], the sensitivity of the sputtering yields to variations from this treatment has not been investigated in these studies. Such variations would effect primarily the transport of the incident light particles, since the energy loss of the low energy target atoms is dominated by the nuclear energy loss mechanism.

For the nuclear energy loss T and the associated scattering angle, use is made of a parameterized analytic formula derived by Biersack et al. [10, 11]. This formula very accurately describes classical scattering for any

repulsive interatomic potential given the particle's energy, impact parameter, and distance of closest approach. The values for the parameters in the scattering formula were determined by a least-squares fitting procedure using precomputed, numerical evaluations of the classical scattering integral [13] based on the Moliere [14] potential. This potential with the Firsov [15] screening length is used for most routine calculations with the TRIM program.

One of the more important attributes of this Monte Carlo approach is that the most realistic interatomic potentials can be readily used. Here, we have calculated the various atom-atom potentials that were necessary using the free-electron approximation as described by Wilson and Bisson [16]. To facilitate the use of these potentials, we adjusted the screening length, in most cases, in the Moliere screening function to give the best fit to the free-electron potentials. For the $\text{Mo}^+ - \text{Mo}^+$, $\text{Au}^+ - \text{Au}^+$, and H-C potentials a better fit was achieved by adjusting the screening length α in the following screening function:

$$\Phi(r/\alpha) = 0.100e^{-0.22 r/\alpha} + 0.472e^{-0.50 r/\alpha} + 0.428e^{-1.51 r/\alpha}, \quad (1)$$

where r is the interatomic separation. This screening function was presented by Wilson et al. [17] in reporting their results for $\text{Nb}^0 - \text{Nb}^0$ potential using the free-electron method. The screening lengths used to fit the screening functions to the potentials are given in Table I together with those of Firsov.

As mentioned above, the impact parameter and the distance of closest approach, in addition to the energy, are needed to use the nuclear scattering formalism. With the pathlength between collisions being $N^{-1/3}$ the impact parameter P is randomly selected using the following formula:

$$P = [R_n / \pi N^{2/3}]^{1/2} \quad (2)$$

where R_n is a random number uniformly distributed between 0 and 1. This assumes there is one atom in the volume element of length $N^{-1/3}$ and base area $N^{-2/3}$. This procedure maintains the atomic density in the target but ignores any correlation between the positions of successive atoms. The distance of closest approach is then obtained, in the usual manner, from the pole of the integrand in the classical scattering integral.

In generalizing the TRIM formalism to follow the target atom trajectories and their subsequent possibility of becoming sputtered atoms, we have set certain criteria for considering the motion and escape of these atoms. This part of the procedure follows closely that defined for the general displacement model in the MARLOWE [9] program. A particle with original kinetic energy E emerges from a nuclear collision with kinetic energy E_1 , after transferring energy T to a target atom, i.e., $E_1 = E - T$. The target atom's motion is considered if the energy T is greater than a threshold energy E_d , and if $T > E_d$, it then loses some binding energy $E_b \leq E_d$. Thus, the final kinetic energy E_2 of a target atom is given by $E_2 = T - E_b$. In the calculations presented here we have set $E_d = E_b$, and the value of E_b depends on whether the collision is with a surface or a bulk atom. In what follows, a model for physically defining the E_b values is presented.

An ion incident upon a metal surface transfers energy to both the surface and bulk atoms of the metal in its slowing down process. This transferred energy may result in the production of surface and bulk vacancies and vacancy clusters as well as the associated interstitial loops. In order to bring a measure of physical understanding to the Monte Carlo calculation presented here and also to provide a predictive capability, a simplified model of these complex radiation damage processes has been developed.

In this model, the incident ions may transfer energy to the "surface" and "bulk" atoms, these two types being the only ones distinguished between. Atoms lying between vacuum and $1/4 a$ (a - lattice parameter) of the surface are considered "surface" atoms and all others are taken to be "bulk." Very real surface complications such as angular orientation, steps, kinks, jogs and effects due to impurities are neglected. Similarly, atoms quite near the surface, i.e., within a few monolayers, are approximated as bulk atoms.

We shall consider the bulk atoms first. The energy required to remove a bulk atom to infinity is denoted E_V^∞ and is given by:

$$E_V^\infty = E_{IV}^F + E_{HS} , \quad (3)$$

where E_{IV}^F is the vacancy formation energy and E_{HS} the heat of sublimation of the solid; E_{IV}^F is the energy required to place a lattice atom on the surface (i.e., to bring it first to infinity and then back to the surface); E_{HS} is the energy per atom to remove an entire layer of the surface to infinity and there dissociate all the atoms of the layer. In forming a bulk vacancy, a lattice atom is brought to infinity and then placed back into an interstitial site, forming a Frenkel pair. The "binding" energy of a lattice atom, E_b , is therefore given by:

$$E_b = E_V^\infty + E_I^F , \quad (4)$$

where E_I^F is the self-interstitial formation energy.

It is recognized that in using Eq. (4) for the binding energy, one is neglecting the dynamics of the process going on. That is, the ejected lattice atom may not actually be in an interstitial position but may create further

knock-ons, and may find itself finally in a substitutional site. Even if it is in an interstitial configuration, that configuration may not be the lowest energy one because the lattice relaxations may not yet have equilibrated. We therefore propose using the equation:

$$E_b = E_v^\infty + E'_I \quad , \quad (5)$$

defining E'_I as an effective interstitial formation energy. Energy E_b is subtracted from the transferred energy T ($= \gamma E \sin^2 \theta/2$) to give the kinetic energy of the ejected particle.

Before turning to the surface atom binding, let us be more specific about the volume dependence of the terms already defined. The vacancy formation energy can be written:

$$E_{1V}^F = - \sum_j V(r_{Vj}^b) + \sum_j V(r_{Vj}^s) + E_{vol} \quad , \quad (6)$$

where $V(r_{Vj}^x)$ is the interatomic potential between a lattice atom at the vacant site in the bulk ($x = b$) or on the surface ($x = s$). (For a first-neighbor two-body potential having magnitude ϕ at the first-neighbor separation, $\sum_j V(r_{ij}^b) = 12\phi$ and $\sum_j V(r_{Vj}^s) = 6\phi$.) Similarly, the heat of sublimation can be written:

$$E_{HS} = - \sum_j V(r_{Vj}^s) - E_{vol} \quad . \quad (7)$$

In Eqs. 6 and 7, E_{vol} is the volume dependent part of the energy, that is, that part of the energy of the lattice which cannot be represented by two-body forces [18]. From Eqs. 6 and 7,

$$E_{vol} = \frac{1}{2} (E_{1V}^F - E_{HS}). \quad (8)$$

We now define E_s^+ to be the energy required to remove a surface atom to infinity and E_s^- the energy required to remove a surface atom and place it in the bulk. Clearly,

$$E_s^- = E_s^+ + E_I. \quad (9)$$

We write

$$E_s^+ = f E_V^\infty - E_{vol}, \quad (10)$$

where f is fraction of the (volume independent) energy required to bring an atom from the bulk to infinity which must be expended to bring an atom from the surface to infinity. Using Eqs. 3 and 8 in Eq. 10, it is easy to show that

$$E_s^+ = E_{HS} + (f - \frac{1}{2}) (E_{1V}^F + E_{HS}). \quad (11)$$

Simple estimates of f can be made by comparing the number of nearest neighbor bonds on a surface (N_s) to the number in the bulk (N_b). For a fcc material, the (100) surface gives $(N_s/N_b) = f = 2/3$, while for a (111) surface $f = 3/4$. The important point to be made is that for any value of $f > 1/2$, it takes more energy (E_s^+) than the heat of sublimation (E_{HS}) to remove a surface atom to infinity. These arguments are consistent with the experimental results of Bay et al. [19] who find that the threshold energies for sputtering appear to be higher than that dictated by the heat of sublimation.

To summarize, if a collision occurs on the surface (depth $\leq 1/4 a$) then $E_b = E_s^+$ for a target atom which will leave the surface on its initial free

flight path L and $E_b = E_s$ for an atom that will have a collision on its initial path. At depths greater than $1/4 a$,

$$E_b = E_{IV}^F + E_{HS} + E'_I. \quad (12)$$

The values of E_{HS} and E_{IV}^F used in the present calculations are given in Table II. Using these values, results for ^4He normally incident on Ni are illustrated in Fig. 1 for $E'_I = 0, 1$, and 3 eV , and for $f = 2/3$ and $3/4$. Note in this figure that the results are not sensitive to the choice of f except at very low energies. A value of $f = 3/4$ was chosen throughout the remainder of this work.

It should be pointed out that a value of 3 eV for E'_I is not unreasonable. Johnson and Wilson [23] found E_I^F to be $\sim 3.3 \text{ eV}$ using a pair potential and non-central force for Ni. Absolute values of formation energies are very difficult to calculate, however, and other pair-potentials may well give widely different results. In bcc materials, interstitial formation energies are usually found to be higher.

3. Results and Discussion

For the Monte Carlo results presented here, a sufficient number of incident particle histories were processed at each energy to yield at least 100 sputtered atoms, and in the majority of the cases this number exceeded 200. Comparisons of repeated calculations with different sequences of random numbers indicated that the statistical errors are approximately 10 to 20 percent. We performed the calculations at energies which correspond closely with those used in the experiments, i.e., $0.05, 0.08, 0.1, 0.15, 0.24, 0.5, 1, 2, 4$, and 8 keV . Most of our comparisons with experimental results are

with the recent data generated by the Garching group [19, 24, 25]. The reader is referred to their original papers for further comparisons with previous results.

The calculated sputtering yields (atoms/ion) already presented in Fig. 1 indicate that $E'_I = 3$ eV is a suitable value for Ni and this value has been used for the other Ni calculations. Fig. 2 shows the calculated results for H, D, T, and ^4He normally incident on Ni together with the experimental measurements of Bohdansky et al. [24] for H, D, and ^4He . Our results show the same energy dependent trends as those of the experiments with the maximum yield in the 1 to 3 keV range. Also, near the maximum yield, the ratios of the ^4He and D sputtering yields to that for H is about the same as determined experimentally. The calculated results at energies above 1 keV are somewhat lower than experiment for ^4He and higher for H and D. Nevertheless, the overall comparison between the calculations and experiments seems encouraging considering our use of the binary collision approximation and the inherent difficulties in measuring small sputtering yields.

Figs. 3 and 4 show our results for D, T, and ^4He normally incident on Au and Mo, respectively. In these figures, we also show the results of Bay et al. [19] for D and ^4He . We again used $E'_I = 3$ eV for Au, but as discussed earlier, this value is expected to be too low for bcc Mo. We therefore show in Fig. 4, the ^4He - Mo results using $E'_I = 3, 10$, and 20 eV and show only the $E'_I = 20$ eV results for T and D. It is felt that $E'_I = 20$ eV may be too high a value to be considered an interstitial formation energy and its necessity may be due to a breakdown of the binary collision approximations. Molecular dynamical calculations are planned to help determine the source of this large E'_I value.

We determine the sputtered atom energy spectra in our calculations, as well as the angular distributions. The angular distributions are all essentially cosine distributions, as is to be expected from our Monte Carlo model, since our targets are amorphous and we consider no influence of surface atoms on the sputtered atoms once they leave the surface. An example of the sputtered energy spectrum is shown in Fig. 5 for 1 keV ${}^4\text{He}$ normally incident on Au. The dashed lines in this figure indicate the variation of the energy distribution in terms of the energy power function E^{-n} with $n = 1.5, 1.8$, and 2.0 . Our results indicate that the spectrum is somewhat harder than E^{-2} as predicted by Sigmund [2], but this is consistent with the recent measurements of Hucks et al. [26] for light ions on Au ($n = 1.8$).

Finally, the calculated sputtering yields for H, D, and T normally incident on C are shown in Fig. 6. Also, the results from three recent experiments are included in the figure. We realize that there are many types of "carbon" and their sputtering properties [4] can vary markedly. Our purpose here is to show the energy dependence of the sputtering yields predicted by the Monte Carlo formalism using nominal values for E_{HS}^* and E_{IV}^F (see Table I) with $E_I^* = 3$ eV. The calculated results indicate that the maximum yield occurs in the energy range from about 0.3 to 0.5 keV. These results disagree with the sputtering yield energy dependence reported by Smith et al. [27] for H, but they are consistent with the measurements of Bohdansky et al. [25] for H and Borders et al. [28] for D.

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TABLE I

Screening Lengths Used in Fitting the Screening Function of Molière and Eq. (1) to the Free-Electron Potentials.

Potential	Screening Lengths (nm)		
	Molière	Eq. (1)	Firsov
H - Ni ⁺	0.0118		0.0137
He - Ni ⁺	0.0101		0.0132
Ni ⁺ - Ni ⁺	0.00819		0.00972
H - Mo ⁺	0.0113		0.0122
He - Mo ⁺	0.0103		0.0118
Mo ⁺ - Mo ⁺		0.00810	0.00849
H - Au ⁺	0.0102		0.0102
He - Au ⁺	0.00928		0.00989
Au ⁺ - Au ⁺		0.00675	0.00699
H - C		0.00160	0.0205
C - C	0.0128		0.0162

TABLE II

Value for E_{HS} and E_{LV}^F

Element	E_{HS} (eV) (a)	E_{LV}^F (eV)
Ni	4.45	1.4 (b)
Mo	6.89	2.4 (c)
Au	3.93	.9 (b)
C	7.38	(2.5) (d)

(a) Metal Reference Book [20]

(b) A. Seeger and H. Mehrer [21]

(c) M. Doyama and J. S. Koehler [22]

(d) Assumed

FIGURE CAPTIONS

Fig. 1 - Monte Carlo calculations of the sputtering yields for ^4He normally incident on Ni for energies less than 10 keV. The parameters f and E'_1 are used in the binding energy formalism (see text). The experimental sputtering yield of Bohdansky et al. [24] are presented for comparison purposes.

Fig. 2 - Calculated sputtering yields for H, D, T, and ^4He normally incident on Ni for energies less than 10 keV. The experimental sputtering yields of Bohdansky et al. [24] for H, D, and ^4He are presented for comparison purposes.

Fig. 3 - Calculated sputtering yields for D, T, and ^4He normally incident on Au for energies less than 10 keV. The experimental sputtering yields of Bay et al. [19] for D and ^4He are presented for comparison purposes.

Fig. 4 - Calculated sputtering yield for D, T, and ^4He normally incident on Mo for energies less than 10 keV. The experimental sputtering yields of Bay et al. [19] for D and ^4He are presented for comparison purposes.

Fig. 5 - Energy distribution of the sputtered atoms for 1 keV ^4He normally incident on Au. The histogram is the calculated results and the dashed lines indicate the energy power function E^{-n} for $n = 1.5, 1.8$ and 2.0.

Fig. 6 - Calculated sputtering yields for H, T, and D normally incident on C for energies less than 10 keV. The experimental sputtering yields of Borders et al. [28], Smith et al. [27], and Bohdansky et al. [25] are presented for comparison purposes. The dashed lines through the experimental H yields are intended only as a visual guides.

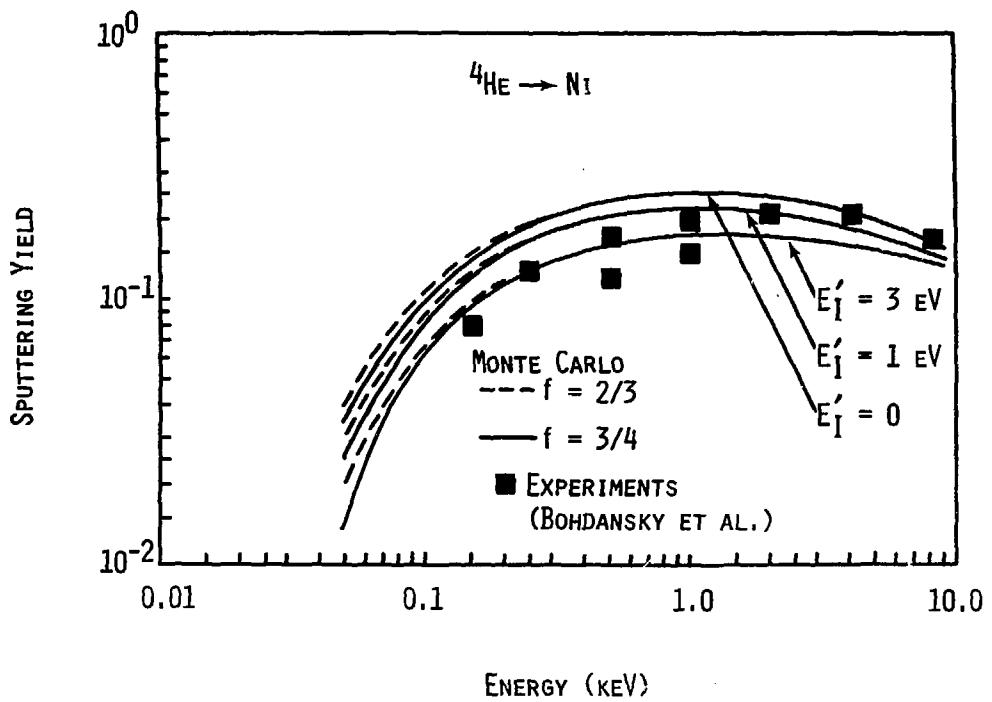


Figure 1

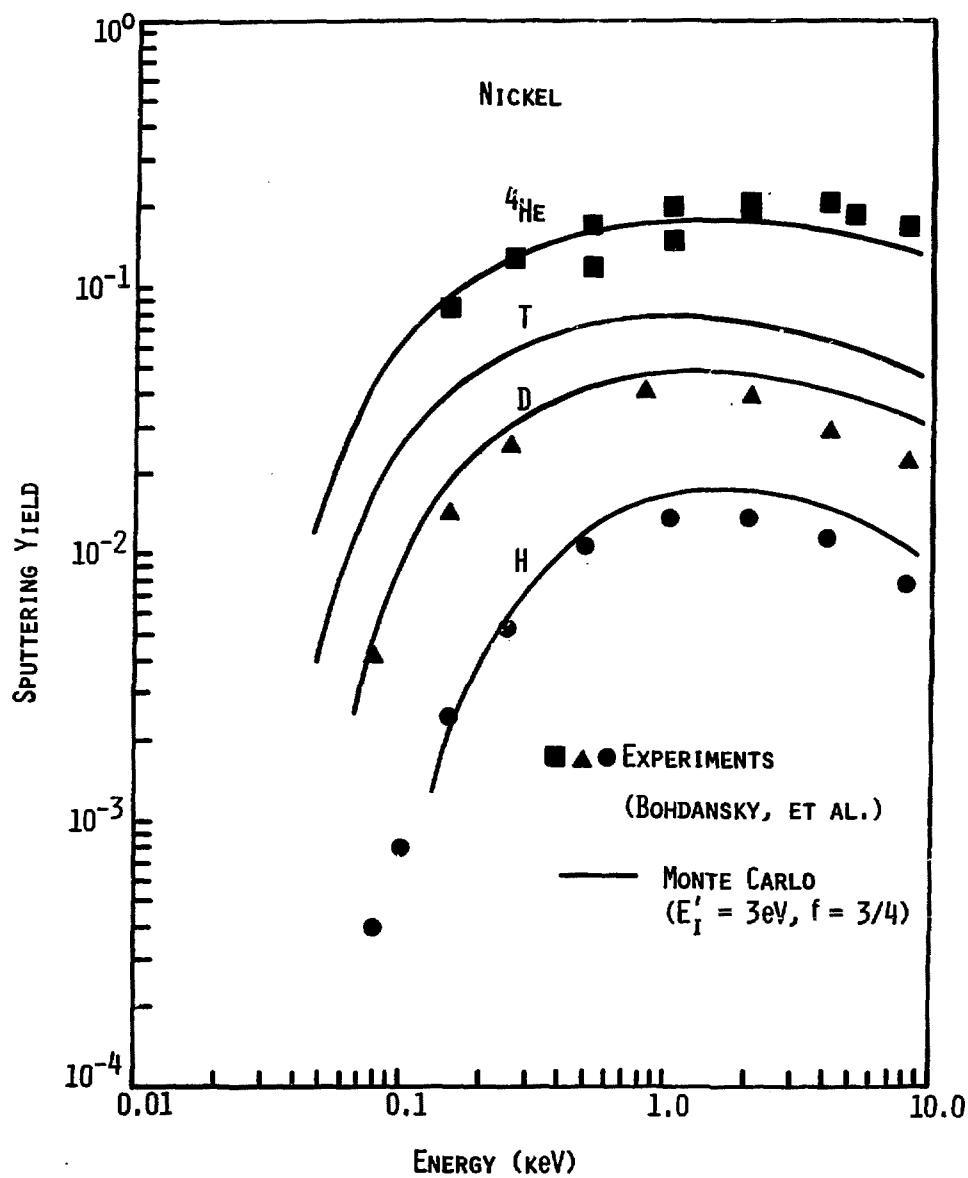


Figure 2

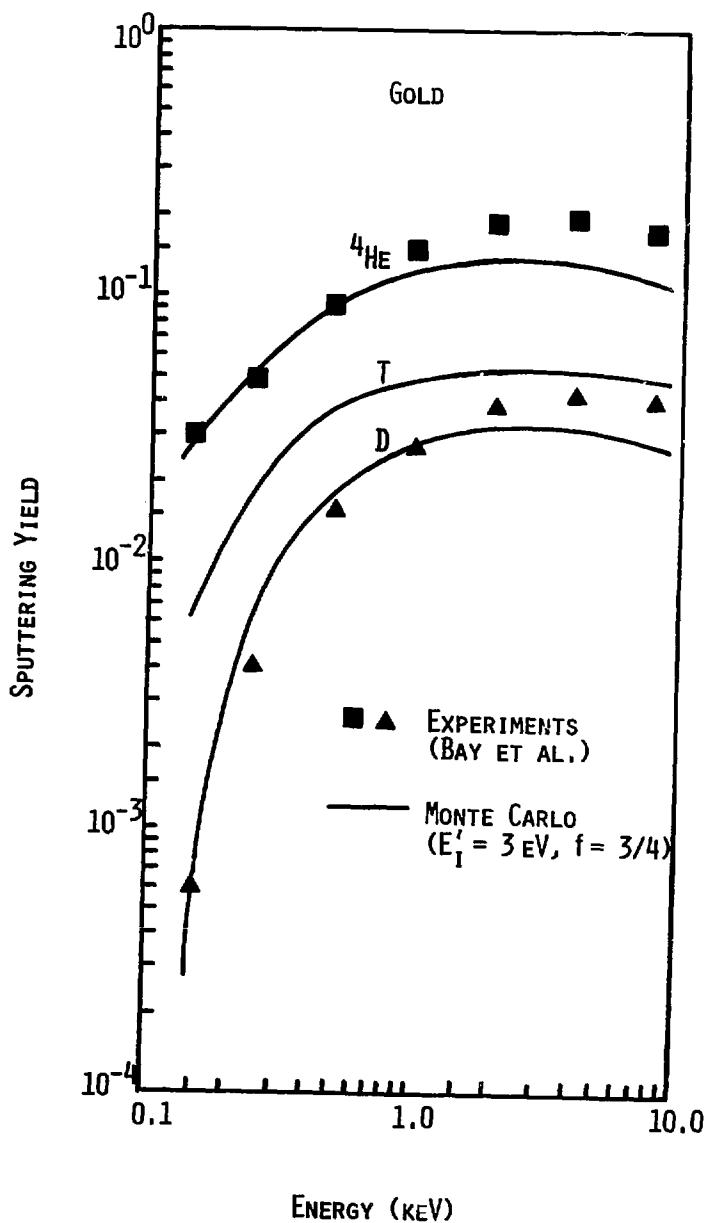


Figure 3

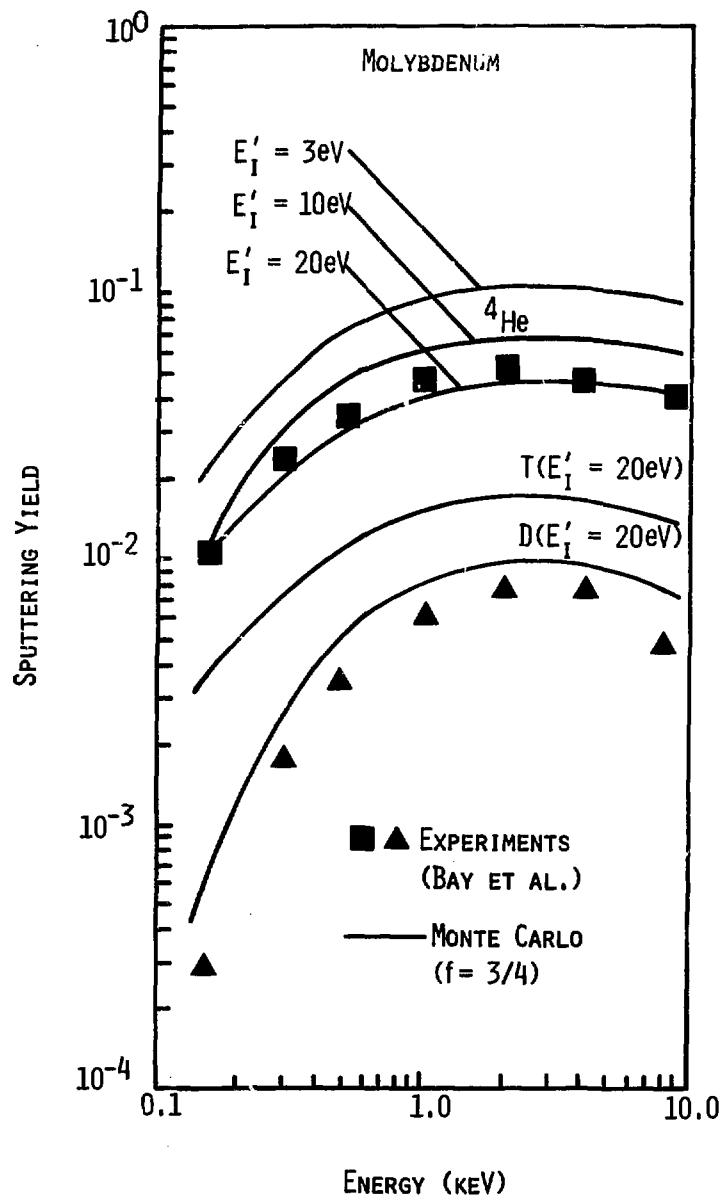


Figure 4

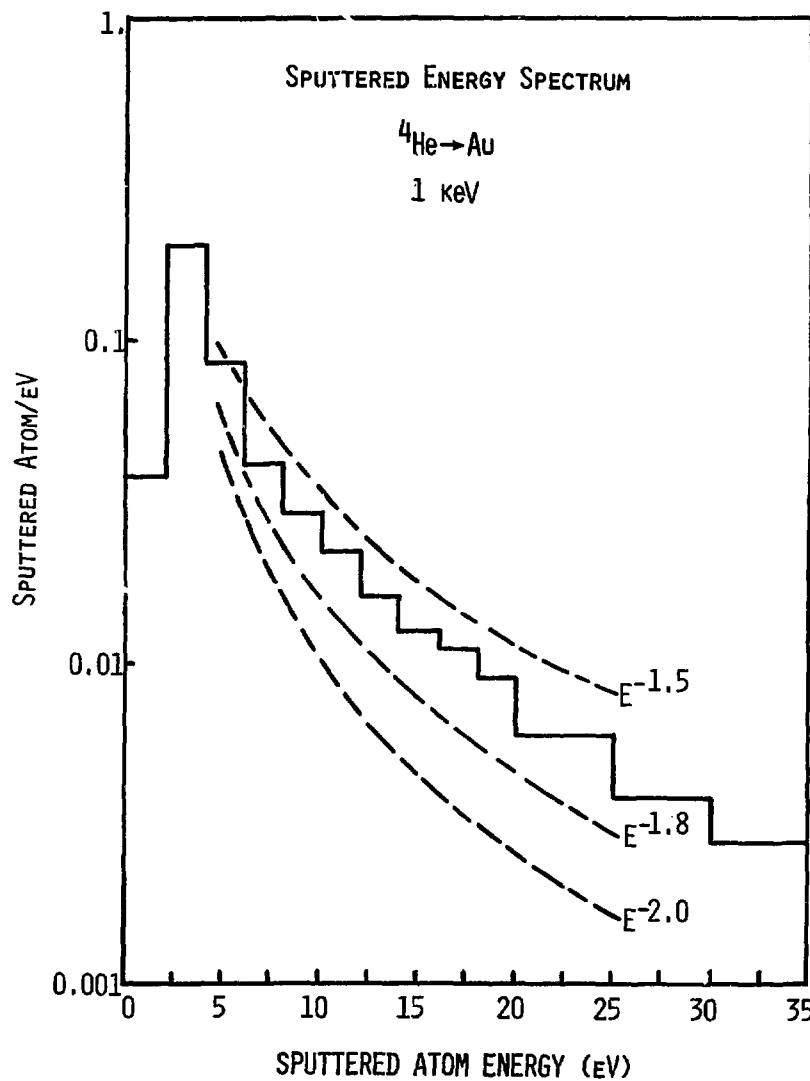


Figure 5

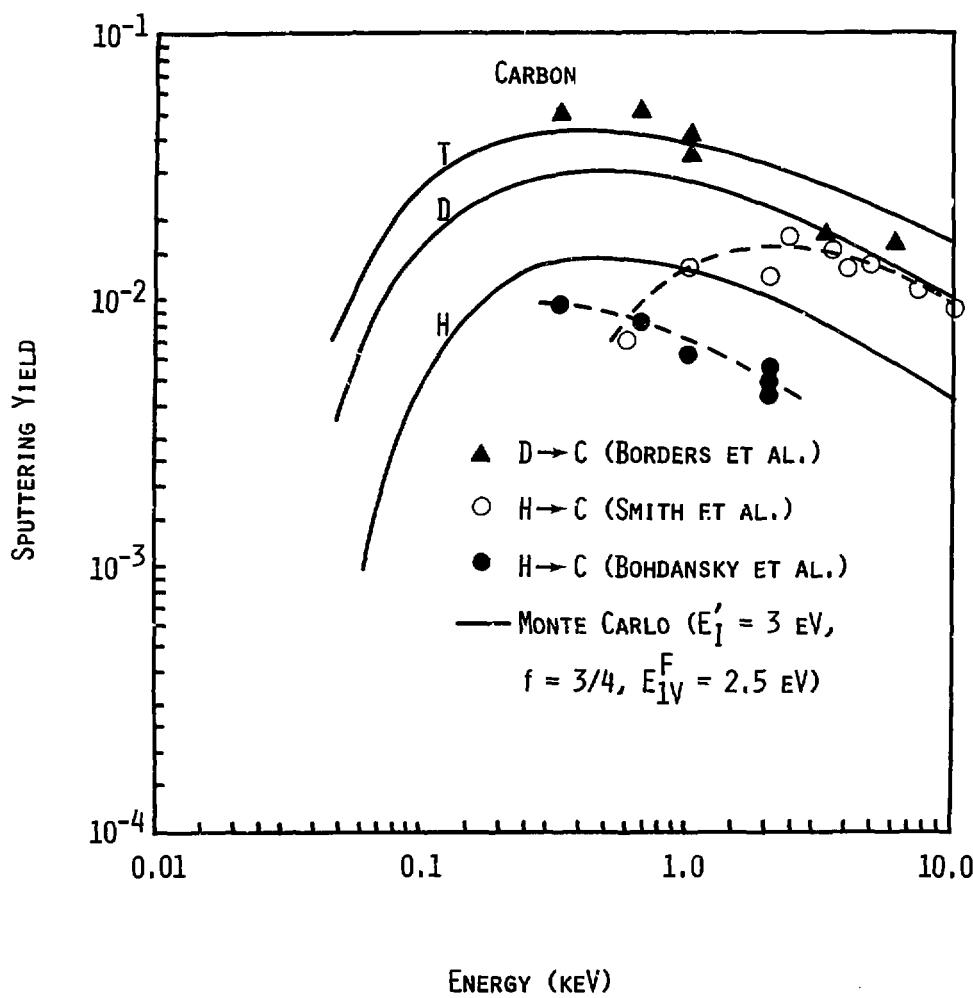


Figure 6