Aust. J. Phys., 1985, **38**, 125–33

Quantum-statistical Analysis of Low Energy Sputtering

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Abstract

Low energy surface sputtering of polycrystalline metals is explained theoretically by means of a three-body sputtering mechanism involving the impinging ion and two metal atoms. By means of quantum-statistical methods, a formula for the number $S(E)$ of atoms sputtered on the average by an ion of energy E is derived from first principles. The theory agrees with experimental sputtering data in the low energy region above the threshold. As an application, mercury–metal atom scattering cross sections are determined by quantitative comparison of the theoretical and experimental $S(E)$ values for sputtering mercury ions from various metals.

1. Introduction

By means of Fermi's golden rule and the statistical density of states concept, the probability $S(E)$ for an atom being sputtered by an ion of energy E incident on a polycrystalline metal is calculated for low ion energies, $E \gtrsim E_0$, above the sputtering threshold E_0. This quantum-statistical theory agrees with experimental sputtering data for low ion energies (Stuart and Wehner 1962; Askerov and Sena 1969). As an application, the formula derived for the sputtering ratio $S(E)$ is used for the determination of the total scattering cross section of mercury atoms (recombined Hg ions) interacting with atoms of various solid metals from experimental sputtering data.

The previous classical sputtering analyses (von Hippel 1926; Henschke 1957; Keywell 1955; Wehner 1956, 1957; Harrison 1961; Garber and Federenko 1964; Behrisch 1964), as well as the modern sputtering theories based on transport theory and Monte Carlo methods [see authoritative reviews by Sigmund (1981), Robinson (1981) and Harrison (1983)], contain phenomenological parameters which have to be determined from experimental data. This difficulty is typical for theories on complicated solid state many-body interactions, which cannot yet be treated in all details from first principles.

A binary collision between a surface atom of the solid and an ion incident normal to the surface can evidently not lead to sputtering since the atom does not acquire a momentum component in the direction of the external normal of the surface. Similarly, binary sputtering is not likely to occur for smaller angles of ion incidence if its energy is not large compared with the sputtering threshold E_0. It is evident that

00004-9506/85/020125$02.00

sputtering, at energies of the order of the threshold, is a three-body process involving one ion and two surface atoms of the solid. At higher ion energies, sputtering will result also from higher order many-body interactions.

By restricting the theoretical considerations to ion energies E of the order of the threshold energy $E \gtrsim E_0$, sputtering is regarded as the result of an ion–atom–atom interaction. Furthermore, it is assumed that the solid is polycrystalline and has a sublimation energy which is on the average $E_s = \langle E_s^{ijk} \rangle$, where the average is taken over the randomly distributed surfaces (ijk) of the crystallites. In this case, the sublimation energy E_s represents the average binding energy of a surface atom of the polycrystalline solid.

In the three-body sputtering process, the incident ion transfers, on average, the energy E_s (as well as kinetic energy) to the atom which is expelled and the energy (α) $2E_s$ or (β) $4E_s$ to the other atom depending on whether the latter is pushed to an (α) unstable or (β) stable interstitial lattice position. Accordingly, the threshold energies for the three-body interactions α and β are

$$E_\alpha = E_s + 2E_s = 3E_s, \qquad E_\beta = E_s + 4E_s = 5E_s.$$

Depending on whether the process (α) or (β) occurs with dominant probability, the apparent threshold [obtained by extrapolation of the experimental $S(E)$ curve, $E \to E_0$] will be $E_0 \approx E_\alpha$ or $E_0 \approx E_\beta$. In the intermediate case, the apparent threshold E_0 appears to be given by the displacement energy

$$E_\gamma = 4E_s.$$

Indeed, some of the experimentally found thresholds E_0 (Stuart and Wehner 1962; Askerov and Sena 1969) are explained by $E_0 = 4E_s$. In other cases, the formulae $E_\alpha = 3E_s$ and $E_\beta = 5E_s$ have to be used to explain the measured thresholds. This is demonstrated in Table 1 which compares experimental and theoretical threshold energies $(E_\alpha, E_\beta, E_\gamma)$ for different metals. Sputtering is, in general, not a simple threshold process which can be defined by means of a single threshold value. This will be shown in detail through the following quantum-statistical considerations.

Table 1. Comparison of experimental and theoretical sputtering thresholds

Target element	Crystal structure	E_0 (theor.) (eV)	E_0 (exp.) (eV)	Target element	Crystal structure	E_0 (theor.) (eV)	E_0 (exp.) (eV)
Ag	fcc	$5E_s = 16{\cdot}75$	17	Nb	bcc	$4E_s = 30{\cdot}84$	32
Au	fcc	$3E_s = 11{\cdot}70$	12	Pt	fcc	$3E_s = 16{\cdot}80$	18
Co	hcp	$5E_s = 22{\cdot}00$	22	Ta	bcc	$3E_s = 24{\cdot}00$	25
Cu	fcc	$5E_s = 17{\cdot}65$	17	Ti	hcp	$5E_s = 24{\cdot}20$	25
Fe	bcc	$5E_s = 20{\cdot}60$	20	W	bcc	$4E_s = 35{\cdot}20$	35
Mo	bcc	$4E_s = 24{\cdot}80$	24	Zr	hcp	$3E_s = 18{\cdot}42$	18

In Table 1, the experimental thresholds have been obtained by extrapolating the data of Askerov and Sena (1969). It is seen that the threshold is in general not equal to $E_0 = 4E_s$, the average displacement threshold in radiation damage. Table 1 shows that the agreement between the theoretical thresholds $(E_\alpha, E_\beta, E_\gamma)$ and the experimental values E_0 (exp.) is excellent, except in the case of Pt. Whether the α

process or the β process is dominant, or both are about equally probable (E_γ), is apparently not dependent on the respective crystal system (fcc, bcc, hcp).

2. Quantum-statistical Probabilities

In general, a sputtering ion recombines with an electron into an atom as soon as it approaches the surface of a metal. This means that the incident ion interacts actually like a neutral atom with the atoms of the solid. This neutralized ion is always referred to as 'ion', in order to distinguish it from the 'atoms' of the solid. Experiments indicate that the atom sputtered from the metal surface is also electrically neutral (Mott and Massey 1965).

When an ion of low energy, as defined above, hits the surface of a solid, one of the following processes may occur: (1) the ion is scattered without energy loss by the bound surface atom it encounters; (2) the ion collides with a surface atom and quasi-simultaneously with a second atom so that three-body sputtering results. The total probability for the ion to interact in either of the two ways with the solid is

$$P_N = N^{2/3}\sigma(E), \tag{1}$$

where N is the number density of atoms in the solid and $\sigma(E)$ is the total (energy dependent) cross section for elastic ion–atom scattering. Let $w_1(E)$ and $w_2(E)$ be the transition probability rates for the processes (1) and (2) respectively. The relative probability with which sputtering occurs is then

$$W_s(E) = \frac{w_2(E)}{w_1(E)+w_2(E)} \approx \frac{w_2(E)}{w_1(E)}, \qquad w_2(E) \ll w_1(E). \tag{2}$$

Combination of equations (1) and (2) yields the sputtering rate, i.e. the number of atoms expelled on the average by one ion of energy E from the solid,

$$S(E) = \sigma(E)\, N^{2/3}\, W_s(E). \tag{3}$$

In principle, $\sigma(E)$ can be calculated quantum mechanically, or determined experimentally (Mott and Massey 1965).

In the transition processes (1) or (2), the ion interacts with the surface of the solid within an area of the extension of the de Broglie wavelength $\lambda = \hbar/(2mE)^{\frac{1}{2}}$. For this reason, the spatial part of the phase space is

$$V = \tfrac{4}{3}\pi R^3, \qquad R \approx \hbar/(2mE)^{\frac{1}{2}}. \tag{4}$$

The transition probability $w(E)$ from a state i to a state f is proportional to the square of the matrix element $|M_{if}|$ and the density of final states $\mathrm{d}\rho/\mathrm{d}E$ per unit energy (Schiff 1955):

$$w(E) = (2\pi/\hbar)|M_{if}|^2 \mathrm{d}\rho/\mathrm{d}E, \tag{5}$$

where

$$M_{if} = \iiint_\Omega \psi_f^* \tilde{H} \psi_i \, \mathrm{d}^3 r, \tag{6}$$

$$\mathrm{d}\rho/\mathrm{d}E = \{\Omega/(2\pi\hbar)^3\}^n \mathrm{d}\Phi(E)/\mathrm{d}E \tag{7}$$

for a state containing n independent particles with moments $\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_n$. Here $\Phi(E)$ is the volume of momentum space corresponding to the total energy E, $\tilde{H}$ is the perturbation (operator) of the Hamiltonian of the ion–atom system which causes the transition i → f, and ψ_i and ψ_f are the wavefunctions of the total system before and after the transition which are normalized for the volume Ω, where $\Omega > V$. Equations (5)–(7) represent the basis for the determination of the process probabilities $w_1(E)$ and $w_2(E)$.

Scattering state. The $w_1(E)$ is defined as the probability rate for the ion to be scattered at the surface of the solid without energy loss. In the centre-of-mass system, the ion momentum is $p = (2mE)^{\frac{1}{2}}$ in the final state and the momentum space volume is $\Phi(E) = \frac{4}{3}\pi p^3$. According to equations (5)–(7), the transition probability for scattering per unit time ($n = 1$) is

$$w_1(E) = (2\pi/\hbar)|M_{if}^{(1)}|^2\{\Omega/(2\pi\hbar)^3\}2\pi(2m)^{3/2}E^{\frac{1}{2}}, \tag{8}$$

where $M_{if}^{(1)}$ is the matrix element of the transition (1).

Sputtering state. The $w_2^{\sigma}(E)$ is defined as the probability rate for the three-body sputtering state with threshold E_σ, where $\sigma = \alpha, \beta$ ($E_\alpha = 3E_s$, $E_\beta = 5E_s$). In the centre-of-mass system, the momenta of the ion (i), the sputtered atom (s), and the second atom (a) can be chosen as

$$\boldsymbol{p}_i = \boldsymbol{p}, \qquad \boldsymbol{p}_s = -\tfrac{1}{2}\boldsymbol{p} - \boldsymbol{q}, \qquad \boldsymbol{p}_a = -\tfrac{1}{2}\boldsymbol{p} + \boldsymbol{q}, \tag{9}$$

so that momentum is conserved $\Sigma_j \boldsymbol{p}_j = \boldsymbol{0}$. Since the potential energy E_σ is expended in the sputtering interaction of type $\sigma = \alpha, \beta$, the total kinetic energy of the three particles is

$$E^* = E - E_\sigma = \left(\frac{1}{2m} + \frac{1}{4M}\right)\boldsymbol{p}^2 + \frac{1}{M}\boldsymbol{q}^2 \geqslant 0, \tag{10}$$

where M is the mass of the target atom. Equation (10) represents an ellipsoid with the axes sections $[4\{mM/(m+2M)\}E^*]^{\frac{1}{2}}$ and $(ME^*)^{\frac{1}{2}}$ in the six-dimensional space of the vectors $\boldsymbol{p}$ and $\boldsymbol{q}$. Hence, the volume of the momentum space is

$$\Phi(E) = \tfrac{1}{6}\pi^3\left(\frac{4mM^2}{m+2M}\right)^{3/2}(E-E_\sigma)^3 \geqslant 0. \tag{11}$$

From equations (5)–(7) and (11) one obtains the transition probability per unit time for the sputtering state with two independent particles ($n = 2$)

$$w_2^{\sigma}(E) = \frac{2\pi}{\hbar}\left(\frac{\Omega}{(2\pi\hbar)^3}\right)^2 |M_{if}^{(2)}|^2 4\pi^3\left(\frac{mM^2}{m+2M}\right)^{3/2}(E-E_\sigma)^2 H(E-E_\sigma), \tag{12}$$

where $M_{if}^{(2)}$ is the matrix element of the transition, E_σ is the threshold, and $H(E-E_\sigma) = 1$ or 0 for $E \geqslant E_\sigma + 0$ or $E \leqslant E_\sigma - 0$ (the Heaviside function).

With the assumption $w_2^{\sigma}(E) \ll w_1(E)$, one obtains, from equations (2), (8) and (12), for the relative sputtering probability

$$W_s^{\sigma}(E) = \frac{\Omega}{8\pi\sqrt{2}}\frac{|M_{if}^{(2)}|^2}{|M_{if}^{(1)}|^2}\left(\frac{M^2}{m+2M}\right)^{3/2}\frac{(E-E_\sigma)^2}{E^{\frac{1}{2}}}H(E-E_\sigma). \tag{13}$$

The square of the matrix elements $|M_{if}^{(1,2)}|$ are proportional to the probabilities for finding the interacting particles in the processes (1) and (2) in the interaction volume V (equation 1), i.e.

$$|M_{if}^{(1)}|^2 \propto (V/\Omega)^1, \qquad |M_{if}^{(2)}|^2 \propto (V/\Omega)^2, \tag{14}$$

since there are one and two independent particles in the interactions (1) and (2) respectively. Substitution of equations (14) and (4) into (13) leads to the following equation for the relative probability for sputtering with threshold E_σ ($\sigma = \alpha, \beta$):

$$W_s^\sigma(E) \approx \tfrac{1}{24} h_{2/1} \left(\frac{(M/m)^2}{1+2M/m}\right)^{3/2} \frac{(E-E_\sigma)^2}{E^2} H(E-E_\sigma), \tag{15}$$

where

$$h_{2/1} = (\Omega/V)|M_{if}^{(2)}|^2/|M_{if}^{(1)}|^2 \tag{16}$$

is a dimensionless coefficient. The matrix elements in $h_{2/1}$ could be evaluated if the force potentials of the interactions (1) and (2) were known. For an individual sputtering event, $h_{2/1}$ would depend on the angle θ which the momentum of the sputtered atom forms with the normal vector of the scattering surface of the respective crystallite.

However, since we are interested in the net observed sputtering probability $W_s^\sigma(E)$ for polycrystalline metals, $h_{2/1}$ has to be averaged for polycrystalline metals with a nearly random spatial orientation of the crystallites. This averaging process is consistent with the use of average sublimation energies $E_s = \langle E_s^{ijk} \rangle$ for polycrystalline metals.

In the following formulation of the observed sputtering rate $S(E)$, the quantities $h_{2/1}$ and E_s represent, therefore, averages or constants for any given ion beam and polycrystalline metal. In this connection, it should be noted that the averages of $h_{2/1}$ and E_s are the parameters which are observed in the sputtering experiments from polycrystalline metals. Furthermore, the experimental data appear to indicate that the dimensionless coefficient $h_{2/1}$ is of the order of 1.

3. Sputtering Ratio

In the sputtering of a surface atom by an ion, the two fundamental cases α and β are distinguished, having the thresholds $E_\alpha = 3E_s$ and $E_\beta = 5E_s$ respectively. We let the probabilities for the occurrence of the thresholds E_α and E_β be g_α and g_β, which are normalized in the usual way:

$$g_\alpha + g_\beta = 1, \qquad g_{\alpha,\beta} > 0. \tag{17}$$

It follows for the relative probability that sputtering occurs with either of the thresholds E_α and E_β:

$$W_s = \sum_{\sigma=\alpha,\beta} g_\sigma W_s^\sigma. \tag{18}$$

Substitution of equations (18) and (15) into (3) yields for the number of atoms sputtered on the average by an ion of energy E:

$$S(E) = \tfrac{1}{24} h_{2/1}\, \sigma(E)\, N^{2/3} \left(\frac{(M/m)^2}{1+2M/m}\right)^{3/2} \sum_{\sigma=\alpha,\beta} g_\sigma \frac{(E-E_\sigma)^2}{E^2} H(E-E_\sigma). \tag{19}$$

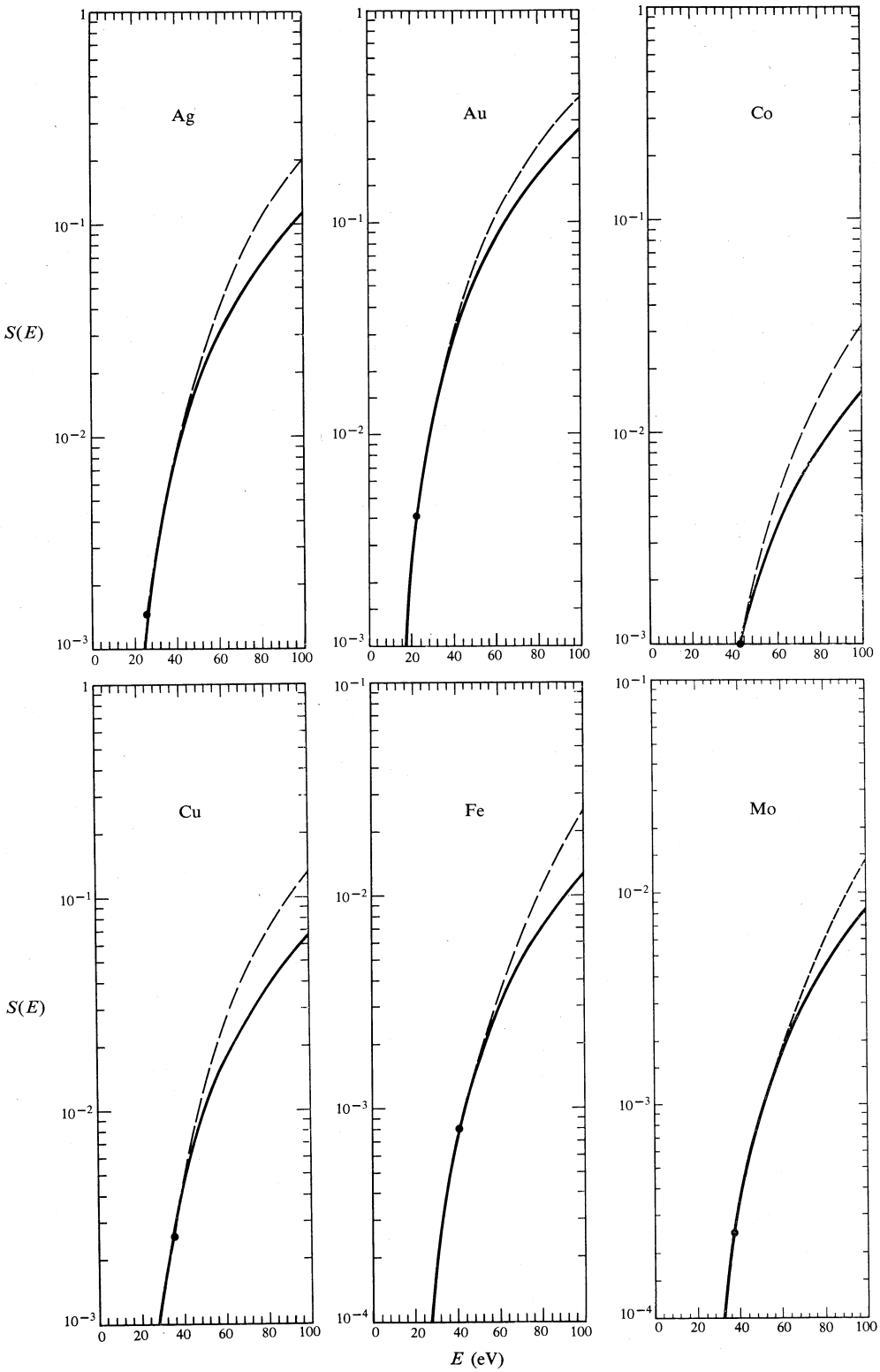

Fig. 1. Theoretical (solid curves) and experimental (dashed curves) sputtering ratios for elements indicated.

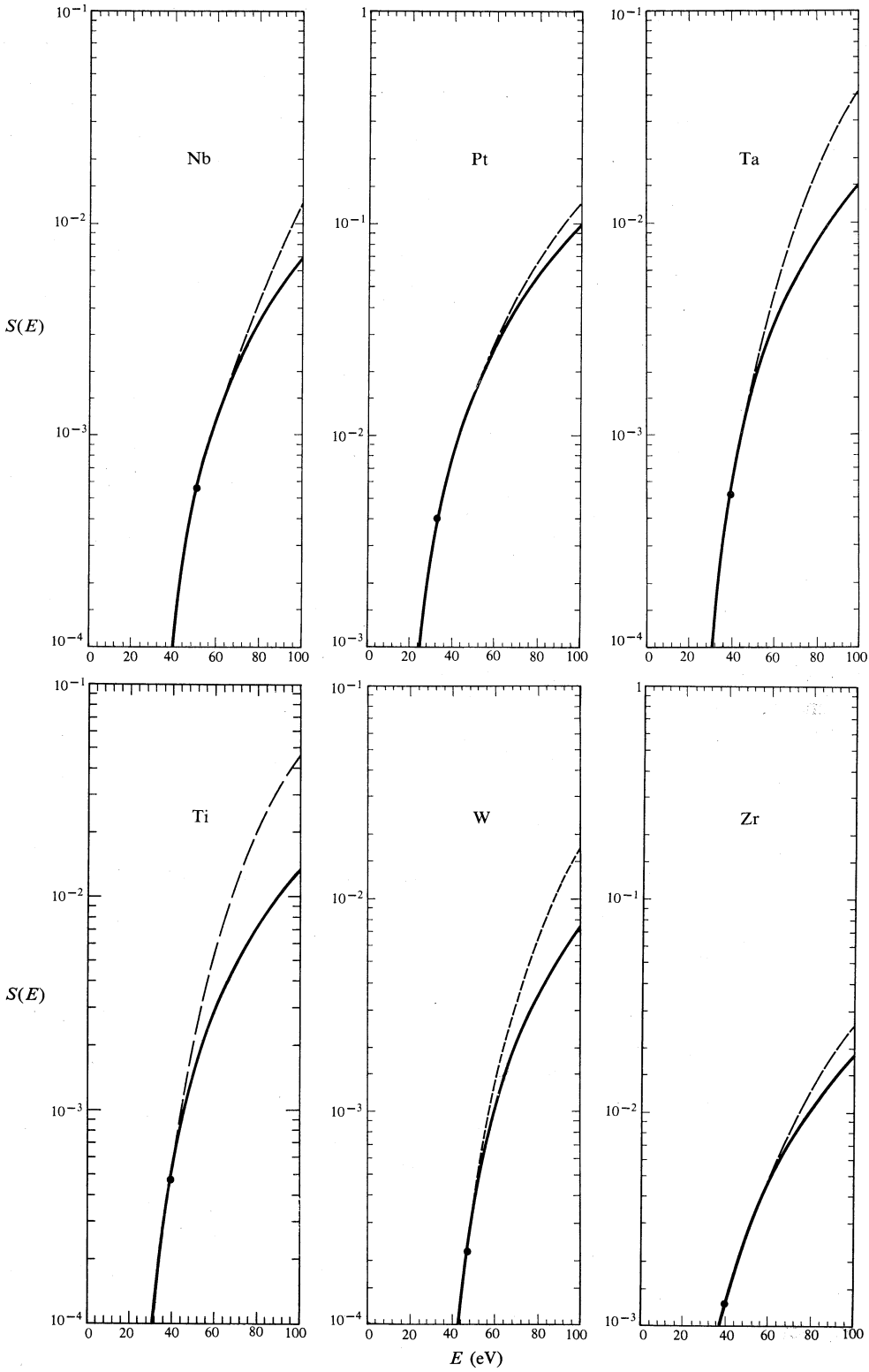

Fig. 1. [*see opposite page*].

For applications, it is suitable to further simplify equation (19), which is strictly valid only for ion energies $E \gtrsim E_{\alpha,\beta}$. For example, if only one threshold $E_0 \in (E_\alpha, E_\beta)$ is important ($g_\alpha \ll 1$ or $g_\beta \ll 1$) and the total scattering cross section $\sigma(E)$ varies slowly at $E \approx E_0$ (absence of resonances), then (19) can be reduced to

$$S(E) \approx \tfrac{1}{24} h_{2/1}\, \sigma(E_0)\, N^{2/3} \left(\frac{(M/m)^2}{1+2M/m}\right)^{3/2} \frac{(E-E_0)^2}{E_0^2} H(E-E_0), \tag{20}$$

with

$$\sigma(E)/E^2 \approx \sigma(E_0)/E_0^2, \qquad E \gtrsim E_0. \tag{21}$$

Equation (20) is of the form of the sputtering relation $S(E) = \text{const.}(E-E_0)^2$, which one finds phenomenologically by fitting the experimental sputtering data. This relation can, therefore, be employed in the extrapolation $E \to E_0$ of experimental data to find the threshold E_0. On the other hand, equation (20) is also useful for predicting the sputtering curve $S(E)$ for polycrystalline metals with known threshold energy E_0 and total scattering cross section $\sigma(E)$. A method for determining the latter has been given by Firsov (1958).

4. Application

In the literature, measurements of the total scattering cross sections for Hg atoms (recombined ions) and target atoms such as Ag, Au, Co, Cu, Fe, Mo, Nb, Pt, Ta, Ti, W and Zr have apparently not been reported. Theoretical cross-section values are not available yet, owing to the mathematical difficulties associated with the application of quantum mechanical scattering theory to complex atoms (Mott and Massey 1965). For these reasons, the cross sections under consideration shall be estimated here by comparing the theoretical (equation 20) and experimental sputtering ratios $S(E)$.

In Fig. 1 the dashed curves represent the experimental sputtering data of Askerov and Sena (1969) for Hg ions and the (polycrystalline) target materials Ag, Au, Co, Cu, Fe, Mo, Nb, Pt, Ta, Ti, W and Zr [with the lowest $S(E)$ value measured at $E = \hat{E}$ indicated by a dot]. The corresponding solid curves are the theoretical values of $S(E)$, based on equation (20) and the theoretical thresholds given in Table 1. The cross-section values $\sigma(E_0)$ are chosen in such a way that the experimental and theoretical sputtering curves agree in the low energy region $E \gtrsim \hat{E}$, since theory and experiment should show best agreement for the lower ion energies in the three-body sputtering model. The mass m of Hg is $200 \cdot 59$ a.m.u., and the remaining constants M and N in equation (20) are given in Table 2. Also shown are the details of the calculation of the cross sections $\sigma(E_0)$ from the experimental sputtering data by means of (20). It is seen that the cross sections $\sigma(E_0)$ for atom–atom scattering are between 10^{-16} and 10^{-15} cm^2 at low energies, i.e. they are of the order of magnitude expected, with $h_{2/1} \sim 1$ (Firsov 1958).

Fig. 1 shows that the theoretical sputtering formula (20) describes the experimental data rather well in the low energy region $E \gtrsim E_0$. The theoretical sputtering curves are plotted up to $E = 100$ eV, in order to show the deviations of (20) from the experimental data at larger ion energies. The three-body sputtering model and the sputtering formula derived from it evidently represent good approximations in the low energy region $E_0 \leqslant E < 10E_0$.

Table 2. Constants of sputtering formula and cross sections $\sigma(E_0)$ for various target atoms

Target atoms	M (g)	Term 1[A]	N (10^{22} cm^{-3})	$N^{2/3}$ (10^{15} cm^{-2})	Term 2[B]	$h_{2/1}\,\sigma(E_0)$ (cm^2)
Ag	$1{\cdot}7906\times10^{-22}$	$5{\cdot}201\times10^{-2}$	5·859	1·509	$8{\cdot}700\times10^{-2}$	$1{\cdot}384\times10^{-15}$
Au	$3{\cdot}2697\times10^{-22}$	$1{\cdot}856\times10^{-1}$	5·903	1·516	$2{\cdot}672\times10^{-2}$	$4{\cdot}230\times10^{-16}$
Co	$9{\cdot}7829\times10^{-23}$	$1{\cdot}268\times10^{-2}$	8·903	1·994	$9{\cdot}687\times10^{-2}$	$1{\cdot}166\times10^{-15}$
Cu	$1{\cdot}0549\times10^{-22}$	$1{\cdot}523\times10^{-2}$	8·468	1·928	$1{\cdot}993\times10^{-1}$	$2{\cdot}480\times10^{-15}$
Fe	$9{\cdot}2706\times10^{-23}$	$1{\cdot}111\times10^{-2}$	8·478	1·930	$7{\cdot}649\times10^{-2}$	$9{\cdot}512\times10^{-16}$
Mo	$1{\cdot}5926\times10^{-22}$	$3{\cdot}998\times10^{-2}$	5·657	1·474	$2{\cdot}248\times10^{-2}$	$3{\cdot}661\times10^{-16}$
Nb	$1{\cdot}5422\times10^{-22}$	$3{\cdot}716\times10^{-2}$	5·187	1·391	$3{\cdot}719\times10^{-2}$	$6{\cdot}417\times10^{-16}$
Pt	$3{\cdot}2385\times10^{-22}$	$1{\cdot}820\times10^{-1}$	6·599	1·633	$2{\cdot}244\times10^{-2}$	$3{\cdot}298\times10^{-16}$
Ta	$3{\cdot}0037\times10^{-22}$	$1{\cdot}563\times10^{-1}$	5·526	1·451	$9{\cdot}593\times10^{-3}$	$1{\cdot}587\times10^{-16}$
Ti	$7{\cdot}9514\times10^{-23}$	$7{\cdot}581\times10^{-3}$	5·659	1·474	$1{\cdot}786\times10^{-1}$	$2{\cdot}908\times10^{-15}$
W	$3{\cdot}0519\times10^{-22}$	$1{\cdot}615\times10^{-1}$	6·324	1·587	$1{\cdot}344\times10^{-2}$	$2{\cdot}032\times10^{-16}$
Zr	$1{\cdot}5143\times10^{-22}$	$3{\cdot}564\times10^{-2}$	4·253	1·218	$2{\cdot}658\times10^{-2}$	$5{\cdot}236\times10^{-16}$

[A] Values for the term $\{(M/m)^2/(1+2M/m)\}^{3/2}$ from equation (20).
[B] Values for the term $\frac{1}{24}h_{2/1}\,\sigma(E_0)N^{2/3}$ from equation (20).

It should be noted that the theoretical sputtering curves are very sensitive towards changes in the thresholds E_0. It can be shown that adequate agreement between the experimental and theoretical sputtering curves cannot be obtained by choosing theoretical thresholds noticeably different from those in Table 1 and varying the values of the cross sections $\sigma(E_0)$. Experimental or theoretical cross-section values are obviously necessary for a more quantitative evaluation of the quantum-statistical sputtering analysis presented.

The main purpose of this theory is to demonstrate that the underlying idea of the phase space dynamics leads to sputtering ratios which agree satisfactorily with the experimental data in the low energy region. This quantum-statistical approach can be further generalized by considering higher order interactions with the solid.

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Manuscript received 5 October 1984, accepted 11 February 1985