

Statistical model for the formation of excited atoms in the sputtering process

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The formation of excited neutral atoms in the sputtering process has not previously been satisfactorily explained. It is shown that a reasonable description can be developed by the consideration of the inelastic energy transfer in the final collision associated with the sputtering of a surface atom. For low enough kinetic energies this inelastic energy transfer is proportional to the kinetic energy given to the sputtered atom. The result is an expression which reproduces in detail experimental measurements of the relative yields of sputtered excited atoms, and gives reasonable agreement with experiment regarding their kinetic energies and absolute yields. The expression equates the yield of the i th state to $2g_i UK \sum_{k=i}^{\infty} G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1})$, where g_i is the degeneracy, U is the surface binding energy, K is the proportionality constant relating the inelastic energy transfer to the kinetic energy, G_i is the cumulative degeneracy (namely, $G_i = g_0 + g_1 + g_2 + \dots + g_i$), and ϵ_i is the excitation energy.

I. INTRODUCTION

When solid surfaces are bombarded with energetic heavy ions, four general categories of target atoms are sputtered. Besides the dominant population of *ground-state neutral atoms*, there are also *ground-state ionized atoms*, well known from their use for surface analysis. Also prominent are *excited atomic species* which are variously neutral or ionized, the use of which for surface analysis is probably less developed than the use for exploring fundamental aspects of the collision process. Finally, there are *molecular species* of various kinds, neutral, ionized, or excited, which again give important insight into the collision process. The total yield S_T of these particles is the sputtering coefficient such as would be obtained from the weight loss of a bombarded target.

The description of these four categories of sputtered particles is most complete in the case of the predominant group, the ground-state neutrals, where the basic results are that the yields^{1,2} S^0 ordinarily scale as the inverse of the surface binding energy U :

$$S^0 \propto 1/U, \quad (1)$$

and the number of atoms (N) with a given kinetic energy (E), i.e., dN/dE , ordinarily has a peaked form which is similar to^{3,4}

$$\frac{dN}{dE} \propto E(E+U)^{-3}. \quad (2)$$

For light incident particles at low energies, one

cannot assume the existence of the collision cascade on which Eqs. (1) and (2) depend, and the resulting expressions⁵ for S^0 and dN/dE are found to be similar but more complicated than Eqs. (1) and (2). A further possibility is recoil sputtering, i.e., a direct interaction of incident particles with near-surface target atoms [Fig. 4(c), to follow], but this can be neglected in the present context as being a minor effect.

The understanding of ground-state ions is less complete, the basic problem being to explain the yields S^+ and S^- for positive and negative ions. Some success has been achieved by Sroubek *et al.*^{6,7} in a quantum-mechanical description of the absolute ion ratio S^+/S_T . Their result was free of arbitrary parameters, though could not be stated in analytical form. Nørskov and Lundqvist⁸ deduced the ratios S^+/S_T and S^-/S_T using a similar quantum-mechanical basis. Their result was analytical and had a reasonable shape although it appears⁷ to give unrealistic values of S^{\pm}/S_T . The understanding of molecules is also incomplete, the basic problem being to explain the yields S_i^M for molecules of the i th type. Limited progress has been achieved, however, for each of the main molecular categories, namely neutrals,⁹⁻¹¹ ions,^{12(a),12(b)} and excited states.¹³

The understanding of excited neutral atoms, which is the subject of this paper, has shown the least progress. An example of the type of difficulty encountered is that the yields S_i^* of excited neutrals in the i th state are observed to have the approximate form

$$S_i^* \propto g_i \exp(-\epsilon_i/\epsilon^*) \equiv g_i \exp(-\epsilon_i/kT^*), \quad (3)$$

where g_i is the degeneracy, ϵ_i is the excitation energy referred to the ground-state as zero, and ϵ^* or T^* are measures of the slopes of plots of $\ln(S_i^*/g_i)$ vs ϵ_i such as those shown in Figs. 1 (Refs. 14 and 15) and 2 (Refs. 16 and 17). Equation (3) is suggestive of thermal equilibrium and some effort has been made to develop thermal-type mechanisms.^{14,18,19} Thermal equilibrium cannot be involved, however, for several reasons, including the experimental results that excited neutrals have very high kinetic energies²⁰⁻²⁵ and that T^* does not show the required variation with ion and target mass.¹⁴

We note finally that the total sputtering yield S_T is given, in the present notation, by

$$S_T = S^0 + S^+ + S^- + \sum S_i^* + \sum S_i^M$$

in units of atoms per ion, provided S_i^M is expressed in units of atoms per ion rather than molecules per ion.

Although there has been little progress in the understanding of excited neutrals, there is a wealth of experimental observations and other details known about these particles.

We will now summarize what is known about

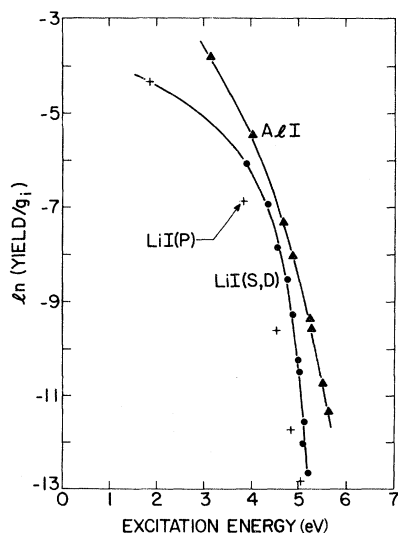


FIG. 1. Relative excited-neutral yields vs the excitation energy plotted according to Eq. (3) for Al bombarded with 12-keV Kr^+ and for Li bombarded with 40-keV Xe^+ . The P states of Li are consistently low. Except for that at 1.85 eV, this result can be understood (Ref. 15) in terms of the decay rate constant γ_i being low so that the photons are in part emitted beyond the viewing region. The Al data are due to Good-Zamin *et al.* (Ref. 14) and the Li data to Jensen and Veje (Ref. 15).

excited neutrals (Sec. II), show how this information eliminates particular models (Sec. III), and then outline a *statistical* model which is relatively successful (Sec. IV). We regard the main alternative to this model as one involving resonance neutralization of sputtered ions into excited neutrals²⁶ and intend to test the two models in work now in progress. A preliminary version of this work is to be found elsewhere,²⁷ while a treatment of excited ionized (as distinct from *neutral*) atoms is in preparation.

II. PROPERTIES OF SPUTTERED EXCITED NEUTRAL ATOMS

The following outlines what is known about sputtered excited neutrals, including both experimental observations and other properties.

(a) They are found²⁰⁻²⁵ to have kinetic energies which have important contributions 1-2 orders of magnitude beyond the target surface binding energy U , indicating that they differ significantly from all other sputtered particles, including ions.²⁷ In terms of the overall kinetic-energy distribution of sputtered atoms [Eq. (2)], excited neutrals would have an important contribution from the high-energy tail as shown by cross-hatching in Fig. 3. (This should not be taken to mean that an abrupt threshold has been demonstrated experimentally.) For example, the excited atoms formed by bombarding Mg, Ca, and Ba fluorides appear, on the basis of the spatial extent of the light that they emit in front of the target, to have contributions from kinetic energies exceeding, respectively, 900, 1600, and 1400 eV.²² In recent studies^{24,25} comparable kinetic energies were obtained from the spatial extent of the light and from Doppler broadening. These two approaches differ in that the latter is free from the basic problem caused by cascade feeding, i.e., from a tendency for the spatial extent of the light to be excessive.

In other work,^{28(a)} using the highly refined technique of Doppler-shift laser-spectroscopy, supposedly excited Zr atoms were found to have normal kinetic energies. The atoms in question were, however, not excited in the usual sense because they differed from the ground state a^3F_2 only in the relative orientation of the S and L angular momenta, whence a^3F_3 and a^3F_4 . Such species would be expected to form with similar probability in the electron pick-up which necessarily occurs when a sputtered Zr ion core evolves into a free neutral atom. In agreement, the observed yields of the three states ($J=2,3,4$) were comparable.^{28(a)}

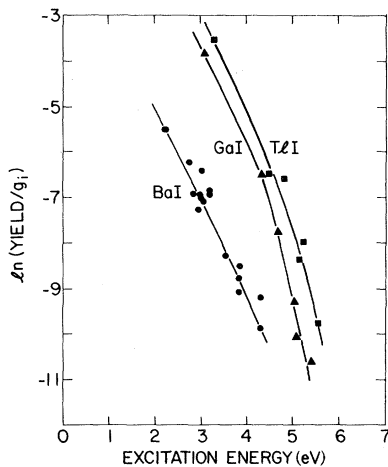


FIG. 2. Relative excited-neutral yields vs the excitation energy plotted according to Eq. (3) for Ba bombarded with 20-keV Ar^+ and for Ga and Tl bombarded with 80-keV Xe^+ . The two Ba points at 4.29 eV were plotted wrongly in the original reference (16) and have been corrected. The Ba data are due to Tsong and Yusuf (Ref. 16), the Ga and Tl data are due to Andersen *et al.* (Ref. 17).

Yu *et al.*^{28(b)} have recently applied the Doppler-shift method to the 1D and 3D states of Ba, which are true excited states, and obtained kinetic energies intermediate between what would be expected from Eq. (2) and what is inferred from the spatial extent of the light.

(b) The relative yields of excited neutrals show an approximately exponential dependence on the

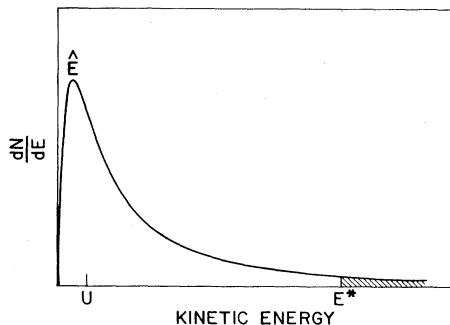


FIG. 3. Sketch of the overall kinetic-energy distribution of sputtered atoms according to Eq. (2). The maximum \hat{E} occurs ideally at $\frac{1}{2}U$, where U is the surface binding energy. Insofar as it is correct to regard E^* as a kinetic-energy threshold for the excitation of sputtered particles (Refs. 20–25), it follows that excited neutrals would lie wholly within the cross-hatched region. If, as is more likely, an abrupt threshold does not exist, the cross-hatched region would simply be an important source of excited neutrals.

excitation energy, as already intimated in Eq. (3) and illustrated in Figs. 1 (Refs. 14 and 15) and 2 (Refs. 16 and 17). Similar approximately exponential dependence has been shown by a wide variety of other systems^{14,18,29} and has an important analog in the relation between ion yields and the ionization potential.^{6,12,30}

(c) The absolute yields of excited neutral *metal* atoms S_i^* from oxidized surfaces³¹ are lower by 2–3 orders of magnitude than those for the corresponding ground states^{1,2,5} or ions.³² Less is known about absolute yields from nominally oxygen-free surfaces, but in the three cases Be,²⁰ Al,³³ and Si,³⁴ it again appears that the excited-neutral yields are distinctly low.

(d) Some of the details of the relative yields of excited neutrals are reminiscent of binary (gas-phase) collisions. This was inferred in one instance from the similarity of plots as in Figs. 1 and 2 but for $\text{Ar}^+ \rightarrow \text{Zn}(\text{solid})$, $\text{Zn}^+ \rightarrow \text{Ar}(\text{gas})$, and $\text{Zn}^+ \rightarrow \text{Zn}(\text{gas})$.^{35,36} In another instance, it was inferred from the similarity of the proportions of S , P , D , and F states for $\text{Xe}^+ \rightarrow \text{Mg}(\text{solid})$ and $\text{Mg}^+ \rightarrow \text{He}(\text{gas})$.¹⁷ To some extent, the evidence for high kinetic energies [item (a) above] is analogous to the energy thresholds well known in binary collisions.^{37,38}

To these four basically empirical observations can be added the matter of size:

(e) Excited neutrals, at least those involving excitation of outer-shell electrons, are an order of magnitude “larger” than the corresponding ground states or ions. This can be shown by considering the mean radii of the electron density in the case of the ground states,³⁹ the subshell³⁹ or crystallographic⁴⁰ radii in the case of ions, and the effective hydrogenic radii, $\langle r^* \rangle$, in the case of excited neutrals. The excited neutrals are thus assumed to resemble hydrogen atoms.⁴¹ If n^* is the effective principal quantum number, defined in terms of the ionization potential I and the excitation energy ϵ_i by

$$\epsilon_i = I - 13.60/n^{*2}, \quad (4)$$

then $\langle r^* \rangle$ is given by⁴²

$$\langle r^* \rangle = (0.7937n^{*2}/Z^*)[1 - l(l+1)/3n^{*2}]. \quad (5)$$

Here l is the orbital angular-momentum quantum number and Z^* is the charge number seen by the excited electron when occupying a large orbital. Values of these various radii are compared in Table I, where for completeness we have also included excited ions.

TABLE I. Sizes of ground and excited states of Al.

Species	Configuration	Effective quantum number n^* from Eq. (4)	Size in Å from Refs. 39 and 40 or Eq. (5)
Al*	$3s^23p$		1.8 ^b
	$3s^24s$	2.19	3.8
	$3s^28s$	6.23	31
	$3s^24d$	3.43	7.8
	$3s^28d$	7.09	38
	$3s^212d$	11.02	95
	$3s^216d$	15.06	178
Al ^{++*}	$3s^2$		< 1.3 ^b
	$3s4s$	2.69	2.9
	$3s8s$	6.73	18
	$3s4d$	3.80	4.9
	$3s8d$	7.79	23
	$3s8g$	7.98	23
Al ^{+++*}	$3s$		> 0.5, < 1.3 ^b
	$4s$	3.09	2.5
	$8s$	7.10	13
	$4d$	3.94	3.6
	$8d$	7.93	16
	$8g$	8.00	15

^aThe sizes given are for triplet states, with singlet states being slightly larger.

^b1.8 Å is $\langle r \rangle$ for the $3p$ electron (Ref. 39). 1.3 Å is $\langle r \rangle$ for the $3s$ electrons (Ref. 39). 0.5 Å is the crystallographic radius of Al³⁺ (Ref. 40).

Not all the experimental or other details known about excited neutrals are as restrictive as items (a)–(e) but they are still important in establishing the form of any expression purporting to describe the experimental yields. These are items (f) and (g).

(f) Yields, at least for S , P , and D states, are approximately proportional to the degeneracy g_i .^{15,17} The information for F states is limited but with a suggestion¹⁷ that the yields are low; there is no information at all on G or H states formed in sputtering experiments. We will subsequently assume degeneracy-proportionality for all states, but would emphasize that this decision normally makes no important difference to the final results. In effect, the relative yields to be calculated for S , P , and D states in Sec. IV B are almost identical with or without allowance for states of the type F , G , H , I , This is because the latter states normally have high excitation energies and are therefore found to be of low yield [cf. Eq. (3)].

(g) Yields do not normally scale as the transition probability A_{fi} , which is an important difference from excited neutrals formed in *plasmas*.⁴³ (We here use the notation f = final, i = initial.) An obvi-

ous qualification is that A_{fi} , or more properly the decay rate constant $\gamma_i = \sum_f A_{fi}$, does enter if the lifetime of the upper state is long compared with the time the excited particle takes in passing the viewing system: yield $\propto \gamma_i$. This, however, is an instrumental and not a physical effect, and the correct conclusion in the present context remains that yields *do not* scale as A_{fi} or γ_i .

The remaining details known about excited neutrals are, at least at present, difficult to relate to mechanisms. These are items (h) and (i).

(h) Yields show a marked correlation with channeling (i.e., azimuthal angle)^{44,45} and with the angle of incidence.⁴⁶ These correlations are of such a nature that they accommodate to a wide variety of mechanisms. For example, yields fall when the ion beam is incident in an open crystallographic direction.

(i) Many yields respond to surface oxygen. The information here is difficult to assess in that it involves responses which are variously either large positive,^{20,33,34} near unity,^{33,47} or negative,⁴⁸ with the reasons for these differences being unknown. This result differs from all other information discussed in this section in that it involves *chemical*

effects. We regard chemical information as being appropriate to a higher-order treatment than will be developed here, and as a step in clarifying the matter have treated elsewhere the nature of the phases formed when metals are implanted with oxygen or nitrogen.⁴⁹

Other kinds of information may turn out in the future to be important but are presently largely unstudied. These are items (j) and (k).

(j) There may or may not be an electronegativity correlation for excited neutrals analogous to that recently discussed for ions.^{50,51} One asks, for example, whether the yield of excited Cu from 1% Cu in Al equals 1% of that from 100% Cu, or whether the possibility of Cu-Al collisions introduces "matrix effects." One asks also whether the oxygen correlation [item (i) above] is just a special case of electronegativity correlation.

(k) Also unstudied is the matter of whether yields depend in any way on the surface binding energy U . There is limited evidence that such a scaling occurs with ions.²⁷

III. THE ALTERNATIVE MODELS

The restrictive nature of some of the experimental observations and physical details discussed in Sec. II serves to simplify the matter of seeking a mechanism for the origin of sputtered excited neutrals. Foremost is the matter of mechanisms involving excitation *within the solid*,^{44,52,53} of which that of Sigmund⁵³ was developed to the extent of including the energy distribution of excited recoil atoms. [The latter was found *not* to be of a threshold type; see also Sec. II, item (a).] Such mechanisms, no matter what the details, run into difficulties firstly by virtue of excited neutrals having sizes of order 4–40 Å (Table I). The accommodation of a *stationary* 40-Å entity such as Al $8d^2D$ in the lattice of solid Al would be by itself a major problem to rationalize. But if the 40-Å entity were moving rapidly, as in the present context, one would have to contend both with the size and with the mean free path for electron loss, of order 0.1 Å (Garcia⁵⁴). Secondly, it has been argued⁸ that excited neutrals inside a solid would have exceedingly short lifetimes owing to level broadening.^{55,56} For example, a level which was broadened to 1 eV would have a lifetime of order $\hbar/\Delta E = 7 \times 10^{-16}$ s. Finally, since 99.5–100% of all sputtered atoms appear to come from the outermost one or two atom layers,⁵⁷ excitation within the solid is largely irrelevant.

Thermal mechanisms where the excitation is acquired *within the solid*^{14,18} are a special case of what was discussed in the preceding paragraph and are therefore ruled out by the same considerations. Such thermal mechanisms are, in addition, incompatible with high kinetic energies. Thermal mechanisms can also be devised, however, where the excitation is acquired *outside the solid*.^{19,58(a)} While large size and short lifetime are now not restrictions, we would suggest that the observation of high kinetic energies again shows the mechanism to be invalid. This is over and above the argument that T^* in Eq. (3) did not show a variation with ion and target mass as would be expected for a thermal event.¹⁴ Specifically, T^* was largely independent of target mass, yet the density of energy deposition increases rapidly with mass.

A recent contribution to the problem of thermal excitation is that of Veje.^{58(b)} He showed that the yield of excited Ag atoms was largely independent of whether the incident particle was Sb^+ , Sb_2^+ , or Sb_3^+ . This was taken as evidence for a collisional mechanism.

A mechanism involving the resonance neutralization of sputtered ions into excited neutrals suggests itself by analogy with what is proposed for excited-neutral formation in the beam-foil process.^{59,60} It also has precedent in models to explain ion yields in terms of electron exchange^{30,61} and in recent work on the formation of excited neutrals and ions from group-II targets.²⁶ We suggest tentatively that this mechanism can be ruled out by virtue of excited neutrals having higher kinetic energies and lower yields than ions. Thus the inequality $E(\text{excited neutral}) \gg E(\text{ion})$ is the *opposite* to what would be expected if excited neutrals were formed by electron pick-up, since pick-up should be enhanced by low kinetic energies. Furthermore, if electron pick-up were occurring it would be reasonable to expect that when a surface was made oxygen-free, the ion and excited-neutral yields would vary in a contrary sense: instead, the inequality $\sum S_i^* \ll S^+$ appears to persist. The mechanism does remain, however, as the main alternative to that to be discussed here and further work is needed.

In a variant of the preceding mechanism, it could be envisaged that excited neutrals are formed *other than* by resonance neutralization but then suffer resonance deexcitation. As a result, the surviving population has high kinetic energies. We will neglect this possibility because it fails to accommodate to the observation that high kinetic en-

ergies are normally found with both metallic and insulating targets,²⁰⁻²⁵ whereas resonance deexcitation should occur only with the former. Exceptions do exist and remain a problem.⁶²

In contrast to the mechanisms just discussed, there is in our opinion no strong objection to a mechanism for excited-neutral formation based on random inelastic energy transfer in the final collision associated with the sputtering of a surface atom. Such a mechanism will be set up in Sec. IV and it will be shown not only that it reproduces information such as that in Figs. 1 and 2 very well, but that it gives reasonable agreement with experiments regarding kinetic energies and absolute yields.

IV. A NEW MODEL BASED ON RANDOM, INELASTIC ENERGY TRANSFER

A. Basic assumptions

Considering the various experimental observations as summarized in Sec. II, together with the matter of the large sizes of excited neutrals (Table I), the depth at which sputtered atoms originate,⁵⁷ and the lifetimes of atoms with broadened levels,⁸ one is led to make the following five assumptions regarding sputtered excited neutrals.

First assumption. A sputtered excited neutral originates from the outermost or next-to-outermost atom layer. It is expelled after being struck from behind by an atom which has a kinetic-energy (E) and angular (θ) distribution scaling as $E^{-2}dE^2 \sin\theta \cos\theta d\theta$. The idea of an origin from the outermost one or two atom layers follows from the simulations of Harrison *et al.*⁵⁷ The energy and angular distribution is well known both from theory and experiment,^{3,4} although the E^{-2} aspect presupposes that cascade sputtering is valid.⁵

For the details regarding the collision of interest, there are at least three possibilities: excitation in a normal cascade-sputtering event [Fig. 4(a)], excitation in a cascade-sputtering event leading to a binary encounter just beyond the surface of atoms which were co-sputtered [Fig. 4(b)], or excitation in a recoil-sputtering event [Fig. 4(c)]. In the first and third cases, there is a fairly good accommodation to the binary-collision nature of the act of excitation, to large sizes (Table I), and to the fact that excited neutrals within a solid would, by virtue of level broadening, have exceedingly short lifetimes.⁸ In the second case, a binary encounter just beyond the surface, the accommodation is complete, although the event is one of low probability. The possible importance of encounters beyond the

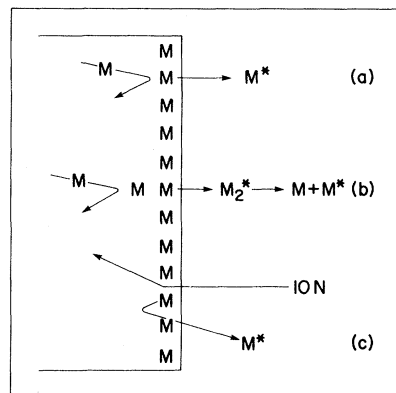


FIG. 4. Sketch of the outermost layer of atoms at the surface of a bombarded solid. In (a) a single atom is shown to be sputtered in a normal cascade event and to acquire excitation in the process. Such an event is similar (though not identical) to a binary collision. In (b) two atoms are shown to be co-sputtered in close proximity. They could be described as undergoing a binary encounter just beyond the surface and any acquisition of excitation would be as in a true binary (gas-phase) collisions. In (c) a single atom is shown to be sputtered in a recoil event and to acquire excitation in the process.

surface was first discussed by Thomas,⁶³ who argued that they might play a role in the matter of excited-neutral yields being enhanced by surface oxygen. Williams³⁰ has discussed them in the context that they might prevent resonant electron transfer with the solid surface, thence loss of excitation. A role for recoil sputtering has been advocated both to explain the high kinetic energies of sputtered excited neutrals⁶⁴ and to explain the increase in kinetic energy with incident energy.⁶⁵

Second assumption. Ideally, the excitation would be described in terms of curve-crossing processes,^{37,38,66} but this is prohibitively complicated to carry out for outer-shell excitations in any but the lightest atoms. Consider, for example, that Al-O interactions involving the ground states and *only one* excited state of each of Al and O lead to 36 potential-energy curves.⁶⁷

We will therefore assume the validity of *random* inelastic energy transfer ΔE_e , such as is observed^{68,69} or calculated^{70,71} to occur for collisions at low kinetic energies E :

$$\Delta E_e \approx KE . \quad (6)$$

Since the proportionality constant is known to be $<< 1$, it follows that Eq. (6) accommodates at least qualitatively to the observation of high kinetic energies and low yields of sputtered excited neutrals.

It may be objected that Eq. (6) contradicts the common experience that the electronic stopping $(dE/dx)_e$ scales as

$$(dE/dx)_e \propto E^{1/2}.$$

This is not so at the lowest energies. In recent ISS work,^{68,69} ΔE_e was found to be $0.20E$ for He^+ impact on Ni (Fig. 5), while in a study⁷² of H , D , and He transmission through thin Au films $(dE/dx)_e$ scaled more nearly as E than $E^{1/2}$ below several keV. As an example of the calculation of a relation of the type of Eq. (6), there is Firsov's⁷⁰ theory of electron exchange for collisions having a small scattering angle. The final result, for colliding atoms having the same atomic number Z , can be written

$$\Delta E_e \approx \frac{0.190(E/M)^{1/2}Z^{5/3}}{(1+0.391Z^{1/2}p)^5}, \quad (7)$$

where E is the kinetic energy of the moving atom in eV, M is the atomic weight of the moving atom in u , and p is the impact parameter in \AA . We are interested in large-angle events and will use the approximation (cf. 73) that p be replaced by \check{r} , the distance of closest approach. Kishinevski⁷¹ used a similar formalism to treat large-angle events and obtained, for the special case that the colliding atoms have the same atomic number and approach head-on,

$$\Delta E_e \approx \frac{0.110(E/M)^{1/2}Z^{5/3}}{(1+0.713Z^{1/3}\check{r})^3}, \quad (8)$$

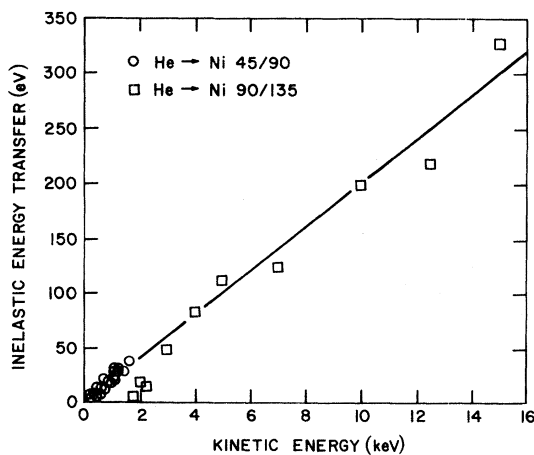


FIG. 5. The inelastic energy transfer ΔE_e determined experimentally for ${}^4\text{He}^+$ scattered from Ni at either $\psi=90^\circ$ (normal) incidence with respect to the surface and a laboratory scattering angle $\theta=135^\circ$ or at $\psi=45^\circ$, $\theta=90^\circ$. A relation of the type $\Delta E_e \approx KE$ is suggested. Due to Eckstein *et al.* (Ref. 68) and Heiland and Taglauer (Ref. 69).

where \check{r} is in \AA . Equations (7) and (8) are compared in Fig. 6 and we note that, for low enough kinetic energies, ΔE_e is more nearly proportional to E than to $E^{1/2}$.

Equations (7) and (8) are based on a model in which a flux of electrons is exchanged between atoms as they pass by each other, the atoms being described in the Thomas-Fermi approximation. The model was subsequently restated⁷⁴ for atoms which are described by the more rigorous Hartree-Fock-Slater model and the magnitude of ΔE_e was found to remain largely as in Eqs. (7) and (8).

We therefore conclude that Eq. (6) is a reasonable description of inelastic energy transfer at low kinetic energies.

Third assumption. To accommodate to the experimental results relating to the degeneracy and transition probability, excited neutrals will be assumed to form with a probability which scales only with the degeneracy g_i . As already discussed in Sec. II, item (f), there is some doubt as to whether states of the type F, G, H, I, \dots show full degeneracy-proportionality¹⁷ but whether or not this is allowed for in the calculations to follow is normally unimportant, at least for low-lying excited states. This lack of importance is a consequence of the high excitation energies, thence low yields.

Fourth assumption. Only this assumption and the one to follow are problematical. In order to accommodate to the experimental result that states

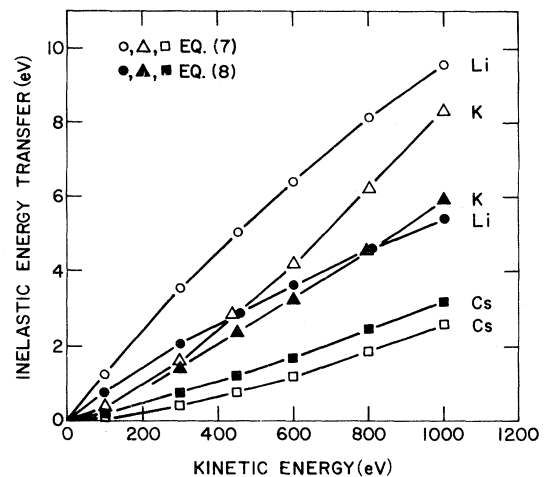


FIG. 6. The inelastic energy transfer ΔE_e , calculated according to the formalism of Firsov (Refs. 70 and 71) by using Eqs. (7) and (8), for the three collision pairs $\text{Li} \rightarrow \text{Li}$, $\text{K} \rightarrow \text{K}$, and $\text{Cs} \rightarrow \text{Cs}$. Note the factor-of-2 numerical similarity of the $\text{Li} \rightarrow \text{Li}$ curve to the $\text{He} \rightarrow \text{Ni}$ curve of Fig. 5. Again a relation of the type $\Delta E_e \approx KE$ is suggested.

with increasing ϵ_i have rapidly and monotonically decreasing yields, it will be assumed that, for a given value of ΔE_e , all states with $\epsilon_i \leq \Delta E_e$ can form. Thus, there need not be exact resonance, $\epsilon_i = \Delta E_e$. This would be rigorous if the energy discrepancy $\Delta E_e - \epsilon_i$ were (for an atom near a solid surface or another atom) rapidly enough converted into kinetic or some other form of energy, but little is known about the rate of such conversion. If it can be assumed further that, not only can all states with $\epsilon_i \leq \Delta E_e$ form, but that they do so with *degeneracy-proportional probability*, then a factor which might be called the *degeneracy ratio* $R_{i,k}$ enters:

$$R_{i,k} = \frac{g_i}{g_0 + g_1 + g_2 + \dots + g_k} \equiv g_i / G_k, \quad (9)$$

where g_0 is the ground-state degeneracy and G_k might be called the *cumulative degeneracy*.

Fifth assumption. As far as the values of ϵ_i and g_i are concerned, they will be approximated as those for free atoms and the fact that the ϵ_i shift and broaden when an atom is near a solid surface,^{55,56} or another atom,⁶⁶ will be neglected. To some extent this approach would be acceptable if the shifting and broadening were such that the free-atom levels retained either their relative spacings (the most favorable situation) or at least their ordering (a less favorable situation).

B. Expression for relative yields

These five assumptions are sufficient to permit an expression for the relative population of the i th state to be written. It is clear that, if $\Delta E_e < \epsilon_i$, the i th state is inaccessible. If $\epsilon_i < \Delta E_e < \epsilon_{i+1}$, then the i th state becomes accessible and should form proportional to

$$(g_i / G_i) \int_{\epsilon_i/K}^{\epsilon_{i+1}/K} E^{-2} dE.$$

(The angular distribution $2 \sin\theta \cos\theta d\theta$ of the atom causing the sputtering can be overlooked provided $\epsilon_i/K \gg U$.) If $\epsilon_{i+1} < \Delta E_e < \epsilon_{i+2}$, then the i th state remains accessible and should form proportional to

$$(g_i / G_{i+1}) \int_{\epsilon_{i+1}/K}^{\epsilon_{i+2}/K} E^{-2} dE,$$

and so on. The final result is easily seen to be that the yield S_i^* is given by

$$S_i^* / g_i \propto K \sum_{k=i}^{\infty} G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1}). \quad (10)$$

This relation disfavors higher levels for two reasons: because G_i increases rapidly and because the level separation $\epsilon_{k+1} - \epsilon_k$ decreases rapidly. Both have as a consequence that there are more and more sinks for the available energy. It is clear that Eq. (10) would remain valid if the free-atom levels (the ϵ_i) were shifted but with the same relative spacings.

Had the fourth assumption not been made, the final result would have been simply

$$S_i^* / g_i \propto \int_{\epsilon_i/K}^{\epsilon_{i+1}/K} E^{-2} dE = K (\epsilon_i^{-1} - \epsilon_{i+1}^{-1}). \quad (11)$$

This relation varies erratically rather than monotonically as ϵ_i increases (Fig. 7).

To evaluate Eq. (10), a list of excited states for each element to be considered was compiled with the help of energy tables.⁷⁵⁻⁷⁸ In each case, sufficient states were taken to make the sum in Eq. (10) well defined (Table II) and all missing singly excited states were interpolated. Levels differing only in J , or having similar excitation energies, were grouped together, so that g_i was given by the appropriate summation.

$$g_i = \sum (2J + 1),$$

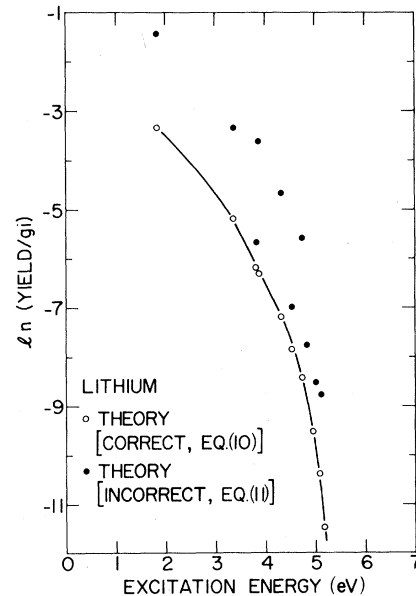


FIG. 7. Comparison of correct theory, Eq. (10), with incorrect theory, Eq. (11), for relative excited-neutral yields due to the bombardment of Li. Correct theory gives an exponential-like curve which decreases monotonically with the excitation energy ϵ_i . Incorrect theory tends to vary erratically with ϵ_i .

TABLE II. The highest excited states used for evaluating Eq. (10).

Element	Highest state used	Internal energy ϵ_i of highest state used (eV)	Ionization potential (eV)	Cumulative degeneracy G_i of highest state used	Ref.
Li	$14p^2P^0$	5.33	5.39	1644	75
Al	$14d^2D$	5.92	5.99	1656	78
Ga ^a	$11d^2D$	5.85	6.00	778	76,79
Ba	$11f^3F^0$	5.09	5.21	1768	77
Tl	$17s^2S$	6.02	6.11	1666	77

^aIn evaluating Eq. (10) for Ga, it is important to take into account the revised F states of Johansson and Litzén (Ref. 79). These states, along with the interpolated G, H, I, \dots states that they imply, lead to a marked increase in the cumulative degeneracy for high-lying excited states.

where J is the total angular-momentum quantum number.

Figures 8 and 9 show the resulting plots of $\ln(S_i^*/g_i)$ vs ϵ_i for the same systems as considered in Figs. 1 and 2. To enable a direct comparison, the experimental results are reproduced with normalization at the positions indicated by arrows. The model is seen to succeed essentially as required: it predicts plots of $\ln(S_i^*/g_i)$ vs ϵ_i which have a similar shape to experiment over a factor of 10^3 in yield and for atomic numbers ranging from

3 to 81. The agreement includes an exponential-like form but with a tendency for convex-up curvature. It should be pointed out that the quantum-mechanical model of Sroubek *et al.*^{6,7} for sputtered-ion formation had a similar degree of success: the prediction of approximate linearity in plots of $\ln(S^+/S_T)$ vs I , where I is the ionization potential, as well as numerically reasonable slopes. In both cases one is thus obtaining Boltzmann-type behavior without any formal assumption of thermal equilibrium.

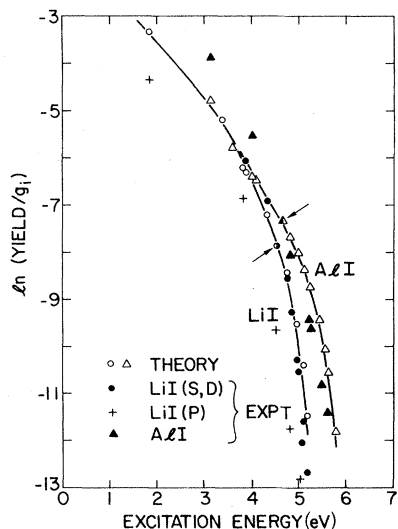


FIG. 8. Comparison of theory, Eq. (10), with experiment for relative excited-neutral yields. The experimental points (Refs. 14 and 15) are the same as those shown in Fig. 1. The positions chosen for normalization are marked with arrows. The agreement is excellent, including the matter of the convex-up shape.

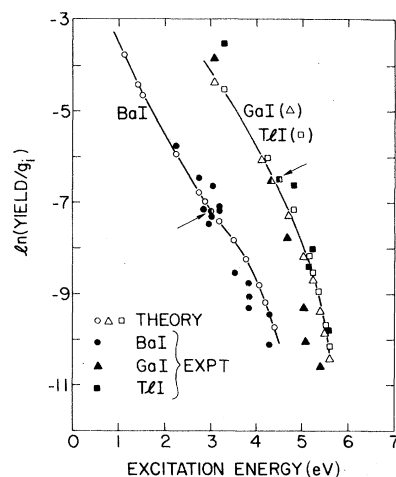


FIG. 9. Comparison of theory, Eq. (10), with experiment for relative excited-neutral yields. The experimental points (Refs. 16 and 17) are the same as those shown in Fig. 2. The positions chosen for normalization are marked with arrows. The agreement with Ba and Tl is reasonable, while with Ga there is an indication that theory is slightly high. This is the usual discrepancy with elements for which the atomic-energy level compilations are incomplete.

C. Expression for average kinetic energy

It would appear that the average kinetic energy $\langle E_i \rangle$ of sputtered atoms in the i th excited state can be described with a similar formalism as the relative yields, the main assumption being that a sputtered atom carries off the kinetic energy of the atom which hits it. If $\epsilon_i < \Delta E_e < \epsilon_{i+1}$, then the contribution to the average kinetic energy is proportional to

$$(g_i/G_i) \int_{\epsilon_i/K}^{\epsilon_{i+1}/K} (E - KE - U)E^{-2}dE \\ \approx (g_i/G_i) \ln(\epsilon_{i+1}/\epsilon_i) .$$

A similar contribution arises for each energy interval and the final result, if divided by Eq. (10), is $\langle E_i \rangle$:

$$\langle E_i \rangle = \frac{\sum G_k^{-1} \ln(\epsilon_{k+1}/\epsilon_k)}{K \sum G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1})} , \quad (12)$$

where the two summations go from $k=i$ to $k \rightarrow \infty$.

Evaluation of $\langle E_i \rangle$ for certain systems that have been studied experimentally²² is summarized in Table III. The calculated values agree roughly with experiment and support the idea that the kinetic energies are unusually high. Too precise a comparison is out of order, however, since the experimental values are subject to a significant uncertainty. First of all, as shown in Table III, the data reduction involves arbitrary forms being taken for the "excitation function," i.e., the function giving the probability that state i forms when the kinetic energy of the collision is E . Second, the experimental values will be excessive whenever cascading is important.

D. Expression for absolute yield ratio

Perhaps the most severe requirement for any model of any aspect of the sputtering process is that it gives reasonable *absolute* yields without the use of arbitrary parameters. This requirement was, for example, met by Sigmund's approach² to S_T , the total sputtering yield for heavy ions, by Littmark and Fedder's approach⁵ to S_T for light ions, as well as by that of Sroubek *et al.*^{6,7} to S^+/S_T , the absolute ion ratio. In the present case, important progress to evaluating the absolute excited neutral ratio S^*/S_T can be made if Eq. (10) is assigned the proportionality constant $2U$.

A simple demonstration of the validity of the constant $2U$ follows from Eq. (2), the normalized form of which is

$$\frac{dN}{dE} = 2EU(E+U)^{-3} \\ \approx 2UE^{-2} .$$

Introducing $2U$ into Eq. (10) we obtain

$$S_i^*/S_T = 2g_i UK \sum_{k=i}^{\infty} G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1}) . \quad (13)$$

In contrast to Eq. (10), Eq. (13) would reflect any shifting of the ϵ_i , even if the relative spacings were retained.

An alternative approach is to sum Eq. (10) over the ground state and all possible excited states, both neutral and ionized. Since the ground state involves $\epsilon_0=0$, it is no longer possible to neglect the angular distribution of the atom causing the sputtering but rather the full distribution must be used:

$$f(E, \theta) dE d\theta = E^{-2} dE 2 \sin\theta \cos\theta d\theta .$$

This means that Eq. (10) is replaced with

TABLE III. Kinetic energies of sputtered excited neutrals.

Target	Transition analyzed	Observed range of kinetic energy thresholds $\langle E^* \rangle$ (eV) ^a	Calculated average kinetic energy $\langle E_i \rangle$ from Eq. (12) ^b
MgF ₂	Mg I, 517.8 nm	290–1170	680; 970
CaF ₂	Ca I, 422.7 nm	510–1580	450; 640
BaF ₂	Ba I, 553.5 nm	920–2350	1100; 880

^aThe method of analysis (Ref. 22) led to kinetic energy *thresholds* rather than average kinetic energies. The range of values corresponds to different assumptions for the "excitation function."

^bThe first value is obtained for K deduced with Eq. (7) and the second for K deduced with Eq. (8).

$$S_i^*/g_i \propto \sum_{k=i}^{\infty} G_k^{-1} \int_0^{\pi/2} \int_{U/\cos^2\theta+\epsilon_k/K}^{U/\cos^2\theta+\epsilon_{k+1}/K} f(E,\theta) dE d\theta. \quad (14)$$

Summing this over the ground state and all possible excited states leads to considerable simplification:

$$\int_0^{\pi/2} \int_{U/\cos^2\theta}^{\infty} f(E,\theta) dE d\theta = 1/2U,$$

while it is easily shown from Eq. (14) that Eq. (10) remains, to good approximation, unchanged. The absolute yield ratio is thus again given by Eq. (13).

The absolute yield ratios for certain systems which have been studied experimentally by Tsong and Yusuf³¹ are summarized in Table IV. Most of the calculated values agree to within a factor of 3 with experiment. The two instances in Table IV of significant disagreement are Zn and Cd, although there is here the possibility that the experimental values are at fault. There is a major problem in

using blackbody light for establishing the quantum yield for a monochromator in the vicinity of 200 nm, the tendency (in our experience) being for quantum yields to be *overestimated* by several orders of magnitude.

IV. DISCUSSION

The theme of this work is that many of the experimental observations and physical details relating to sputtered excited neutrals are so atypical of sputtered particles that they provide important mechanistic hints. In particular, the mechanism must be one which involves high kinetic energies and this immediately rules out a role for thermal events, whether inside or outside the solid. The

TABLE IV. Absolute yield ratios of sputtered excited neutrals.

Element	Transition analyzed (nm)	Observed absolute yield ratios ^a (atoms/atom)	Degeneracy g_i	K^b	Calculated absolute yield ratios from Eq. (13) ^c
Ag	328.1	0.010	4	0.012	0.0041
Al	396.2	0.0039	2	0.0093	0.0019
Ba	553.5	0.0014	3	0.012	0.0018
Be	234.8	0.00022	3	0.0042	0.00069
Ca	422.7	0.0030	3	0.010	0.0016
Cd	228.8	0.00021	3	0.012	0.0016
Cs	455.5	0.0046	4	0.012	0.0013
Ge	303.9	0.00075	3	0.011	0.00060
In	451.1	0.0041	2	0.012	0.0037
Li	670.8	0.0084	6	0.0042	0.012
Na	589.0	0.0074	4	0.0086	0.011
Ti	365.3	0.00018	11	0.010	0.00015
Tl	351.9	0.0047	6	0.013	0.0015
Zn	213.8	0.000009	3	0.011	0.0013

^aThe values given by Tsong and Yusuf (Ref. 31) have been divided by the branching ratio where appropriate, namely with Al and In. The targets used were NBS glass standards SRM 611 and RM 30.

^b K was deduced from the equation (Ref. 71) corresponding to Eq. (8) but with allowance for $Z_1 \neq Z_2$. The moving atom was taken as oxygen and the struck atom as the relevant metal.

^cThe surface binding energy U was taken as 6.4 eV, which is the heat of atomization of SiO_2 (Ref. 80).

fact that excited atoms have large sizes and (at least within a solid) short lifetimes rules out formation *within* the solid. The inequalities $E(\text{excited neutral}) \gg E(\text{ion})$ and $\sum S_i^* \ll S^+$ tend to rule out resonance neutralization of sputtered ions into excited neutrals, although this mechanism does remain as the main alternative to that discussed here. Finally, arguments can be made suggesting that resonance deexcitation is unimportant.

It is easily shown that random, inelastic energy transfer is a very inefficient process. Kinetic energies of several 100 eV give inelastic transfers, ΔE_e , of only 2–5 eV, which is of the order of an excitation energy. The detailing of a model based on ΔE_e is thus an obvious and simple way to explain what are the most problematical aspects of excited neutrals, the high kinetic energies and low yields.

To develop the model it is found sufficient to introduce five assumptions, the first three of which have a firm basis in experiment or theory. They are (1) that a sputtered excited neutral is an outer-layer atom which is struck from behind by atoms having kinetic energies distributed as E^{-2} . (2) The inelastic energy transfer ΔE_e is related to the kinetic energy E as $\Delta E_e \approx KE$, where K is a known constant and is $\ll 1$. (3) The probability of a given excited state scales with the degeneracy g_i but not the transition probability A_{fi} . (4) For a given value of ΔE_e , any excited state with $\epsilon_i \leq \Delta E_e$ can form, and (5) the quantities ϵ_i and g_i have values appropriate to free atoms.

The final result is that one can write the following expression for the yield of excited neutrals

from a sputtered surface:

$$S_i^*/g_i \propto K \sum_{k=1}^{\infty} G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1}), \quad (10)$$

where G_i is the cumulative degeneracy [Eq. (9)]. This relation predicts plots of $\ln(S_i^*/g_i)$ vs ϵ_i which, provided a proper normalization is made, have a similar shape to experiment over a factor of 10^3 in yield and for atomic numbers ranging from 3 to 81. The agreement includes an exponential-like form but with a tendency for convex-up curvature.

Closely related are expressions for the average kinetic energy [Eq. (12)] and the absolute yield ratio [Eq. (13)] of sputtered excited neutrals. The agreement between experiment and theory is good in both cases, a result which is particularly remarkable in the case of absolute yield ratios.

We regard the major unresolved (or partly resolved) problems relating to excited neutrals as including the question of the extent to which yields scale as the degeneracy. It must be borne in mind that the scaling, however reasonable, appears to be only partial.¹⁷ Another problem is to develop an understanding of the yields of species which are both ionized and excited, a matter in which there has been little progress except for the work of Veje.²⁶

At a later time it might be possible to comment on the effect of surface oxygen. This problem is not wholly amenable to the present model in that it involves a description of the chemistry of the target surface and the present model is wholly statistical in nature.

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