

Section I. Theory of sputtering and molecular scattering

MECHANISMS AND THEORY OF PHYSICAL SPUTTERING BY PARTICLE IMPACT

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This article summarizes theoretical work on sputtering during the past decade, with the emphasis on elemental sputtering in the linear cascade and spike regimes as well as alloy sputtering. The sputtering of molecules and clusters, and electronic sputtering of insulators and biomolecular materials are discussed more briefly, and topics like charge and excitation states of sputtered particles as well as surface topography are left out, in view of contemporary summary papers in this issue and elsewhere. The paper is nontutorial and assumes some general knowledge of the field on the part of the reader, based e.g. on ref. [1] or ref. [2]. The discussion emphasizes principles and methods as well as open problems rather than quantitative results. A few general recommendations for efficient utilization of computer simulation conclude the paper.

1. Introduction

I have been asked to summarize major developments in the theory of physical sputtering that have taken place since the time of the first workshop in this series which was held ten years ago. At that time, the organizers had given me a similar task, and I did not find it very difficult, more or less by memory, to condense on 32 pages what I thought were some essentials of sputter theory [1].

Now, in 1986, I find myself in quite a different situation. During the past ten years, sputtering has developed into a wide field of research, both with regard to the variety of observable physical phenomena, the underlying processes, applications in research and technology and, not the least, the number of active people involved. Since ten years' literature on the topic of this contribution comprises several hundred items, I find it impossible within the given limits to present a comprehensive and perhaps even a fair review. On the other hand, there are three monographs on the field of sputtering [2–4] and several recent surveys on sputter processes and theory, written from a variety of viewpoints [5–12]. Moreover, major subfields of sputtering are covered by other reviews at this workshop or at the 1986 symposium on sputtering [13]. Evidently, I shall avoid duplicating that information and instead try to trace trends and connections, point at key problems, contribute to clarifying existing controversy and probably generate new one.

On the experimental side, the past decade has seen a major impact of ultrahigh vacuum techniques and surface analysis on the field of sputtering. At the same time, laser techniques have greatly expanded the possibilities of studying sputter processes. These and many other developments initiated a new generation of sputter experiments.

On the theoretical side, sputtering may probably still be categorized as an atomic collision phenomenon, but its interrelations with solid state and surface physics, materials science, and atomic, molecular, and chemical physics have become much more obvious. Not the least this series of workshops has contributed substantially to the interdisciplinary character of current sputter research.

Here is a list of active subfields in sputtering, several of which were almost unknown ten years ago. Note that the list refers only to *basic processes in sputter erosion*.

(1) Electronic sputtering, i.e., surface erosion due to electronic excitation or ionization. Known long ago for alkali halides and a few luminescent materials, the phenomenon can now be observed on a wide variety of insulators, occasionally with spectacular yields [14–19].

(2) Sputtering of molecules and clusters. The (usually small) ionic component of the sputtered flux has long been known to contain clusters and molecules. It appears now that the emission of both small and large clusters as a noticeable component of the sputtered flux is more the rule than the exception, and that both small and large molecules can be ejected intact [17,18,20–25].

(3) Sputtering of alloys and compounds. Common understanding was infinitesimal a decade ago. Sometimes it looks as if it still is. But the amount of accumulated experimental data is truly impressive, and so is the variety of physical processes that need to be considered in the analysis [26,27].

(4) Exotic target materials. Metal and semiconductors used to dominate. Nowadays, targets investigated range from condensed gases, planetary atmospheres, and lunar dust grains to proteins and viruses [17,21, 28–30].

(5) High-density cascades (spikes). This was a field in progress ten years ago and attracted much attention subsequently. In addition to elastic-collision spikes, also

spikes with a high density of electronic energy deposition play an important role [1,31,32]. Some clarification has been achieved, but much is left to be done.

(6) Low-density (“linear”) cascades. This used to be the main object of sputtering studies. There is sufficient common consensus about physical processes and theoretical principles to justify discussion of quantitative details and of characteristic differences between various theoretical approaches. Most computer simulations of the sputter process address this area [1,5–11,33].

(7) Charge and excitation states of sputtered particles. Progress in this field has undoubtedly been stimulated decisively by discussions in this series of workshops [34–39].

In trying to find some common trend in basic studies of sputter erosion, I find that during the period of 1955–65, the phenomenon was identified and explored as an atomic collision phenomenon, mostly by a variety of experiments involving metallic single crystals. In the following decade, the gross features of the energy deposition process and its relation to sputtering were analyzed along with progress in ion implantation, and during the past ten years, attention has increasingly been directed toward studies of sputter emission on an atomic scale. The latter feature shows up in fairly detailed models for the ejection mechanism, the depth of origin of sputtered particles, the role of segregation layers, the electronic states as well as the states of aggregation of emitted particles, angular desorption patterns, and more.

With regard to the present contribution, the main emphasis will be laid on topics 3, 5, and 6 which are not covered by other surveys in this symposium. For reasons of a logical presentation, they will be discussed in reverse order. Other topics will be touched upon, more or less, but for more balanced surveys, the reader is referred to other contributions in this volume as well as the references given above.

2. Knockon sputtering, low energy deposition density

This section addresses linear cascade sputtering, taken in a broad sense. A collision cascade is linear if only a minor fraction of the target atoms within the cascade volume is set in motion. For a bulk cascade, this implies a low density of point defects generated. With respect to sputtering, it implies that the sputter yield must be small compared with the number of target atoms located within the surface area affected by a bombarding particle. In practice, cascades in metals and semiconductors are close to linear except those generated by rather heavy ions bombarding heavy targets in the energy range from ~ 10 keV to ~ 1 MeV [1,5,40,41]. More to follow in section 3.

Linear cascades may be described by linearized

transport equations of the Boltzmann type [5,42]. Monte Carlo simulations of the TRIM type [43,44] are inherently linear. In both types of approach, energy and momentum are conserved while particle number is not.

Binary collision codes of the MARLOWE type [6,45] conserve particle number and therefore have a built-in linearity test, although existing codes of this type are unable to simulate nonlinear cascades where collisions between moving atoms are frequent events. Molecular-dynamics codes produce apparently nonlinear cascades because of the absence of a threshold for atomic motion [11,46]. This nonlinearity does not necessarily imply a major influence on the sputter process as will be seen in section 2.1.

In ref. [5], it was found convenient, in addition to the linear and nonlinear cascade regimes, to separately consider a single-knockon regime covering low-energy and light-ion sputtering. This is evidently part of the linear cascade regime, but it is not well described by the conventional solution of the Boltzmann equation [47]. This limitation is irrelevant for simulation codes and some alternative solutions of the transport equation. Therefore, the single-knockon regime will not be singled out in this survey.

For reference purposes, consider the linear sputter yield formula [47,5]

$$Y = \Lambda F_D \quad (1)$$

with

$$F_D = \left(\frac{dE}{dx} \right)_n \alpha \left(\frac{M_2}{M_1}, \theta_0, E \right) \quad (2)$$

and

$$\Lambda = \frac{\Gamma_m}{8(1-2m)} \frac{1}{N C_m U^{1-2m}}, \quad (3)$$

where F_D is the energy deposited per unit depth at the sputtered surface, $(dE/dx)_n$ is the stopping power for elastic collisions, α is a dimensionless function of the target/ion mass ratio M_2/M_1 , the angle of incidence θ_0 and the primary energy E of the ion, and Λ is a material constant containing the planar surface potential U , the number density N , cross section parameters m and C_m , and a dimensionless quantity Γ_m dependent on m . Moreover, the equivalent energy spectrum reads [5,48]

$$Y(\theta, \epsilon) d^2\Omega d\epsilon \propto \frac{\epsilon}{(\epsilon + U)^{3-2m}} \cos \theta d^2\Omega d\epsilon, \quad (4)$$

where ϵ and θ are the ejection energy and angle against the surface normal.

Eqs. (1)–(4) have undergone extensive experimental testing. With regard to the dependence on beam parameters, successes and failures of eq. (2) have been known for a while [1,5,40,49]. Progress in this area will be mentioned briefly. More emphasis will be put on the

target properties, eq. (3), as well as to energy spectra, eq. (4).

2.1. Improving predictions of linear cascade theory

The physical model underlying Monte Carlo simulation codes [43,44,50] is roughly equivalent with linear transport theory. Therefore, predictions of the latter can be tested by an alternative theoretical approach, and specific problems can be solved where progress in transport theory is slow because of analytic complexity (e.g. grazing incidence, light-ion and low-energy sputtering). While Monte Carlo codes are reasonably transparent and easy to handle, achieving sufficient statistics is often a problem. Moreover, it seems difficult to extract general scaling laws in the absence of guidance from transport theory.

By and large, there is good agreement between Monte Carlo and transport theoretical results wherever to be expected, i.e., *for equivalent input regarding interatomic potentials, binding energies, and electronic stopping*. The latter precaution is important but often ignored.

One reason for the success of the TRIM code has little to do with the simulation code though with the ion-atom potential. Fig. 1 shows a comparison between sputter yields for $\text{Kr}^+ - \text{Cu}$ and eqs. (1)–(3), for $m = 0$, taken from ref. [47], with the only change that $(dE/dx)_n$ was replaced by the stopping power function of ref. [51]. Although $\text{Kr}^+ - \text{Cu}$ is already well described by a combination of Thomas–Fermi [52] and Born–Mayer [47,53] potentials, the potential of ref. [51] is superior toward low energy (down to ~ 300 eV), and it illustrates more suggestively the presence of a spike component near the maximum.

The systematic error of the Thomas–Fermi interaction at low energies has long been known [54,55], and the consequences for sputter yield predictions have been pointed out repeatedly [56–58].

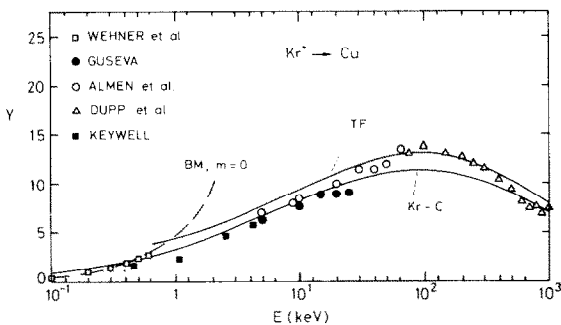


Fig. 1. Sputter yield of copper for krypton ions versus ion energy at perpendicular incidence. Theoretical curves BM, $m = 0$, TF, and Kr-C refer to Born–Mayer and Thomas–Fermi ion–target interaction [47] and the potential of Wilson et al. [51], respectively. For references to experimental data cf. [47].

The credibility of molecular dynamics simulations was hampered severely for many years by the application of an unusually awkward ion–atom potential function resulting in unrealistic predictions for the sputter yield [11,59–63]. The ice was broken slowly in 1980 when the influence of the ion mass and ion–target potential were investigated separately [64–66]. Not surprisingly, the results fit very well with the predictions of linear transport theory (fig. 2). Caution is indicated with regard to the validity of earlier results. Although it was found that only the magnitude of the yield depends on the ion–atom potential while differential quantities should be unaffected [64,65], a result that is obviously consistent with eqs. (1)–(4), the decoupling expressed by these relations is known from experiment to more or less break down at the low energies (≤ 1 keV) where many molecular dynamics simulations have been performed [5]. The main lesson is, however, that molecular dynamics simulations are capable of providing good estimates of the sputter yield (and of other measurable quantities) and that, as in the case of any other theory, their validity needs to be tested *also* against experimental yields. I find it surprising for how long a period such an obvious scientific requirement was denied [11,63,64].

A key quantity in eqs. (3) and (4) is the parameter m , $0 \leq m < 1$, which is related to the steepness of the

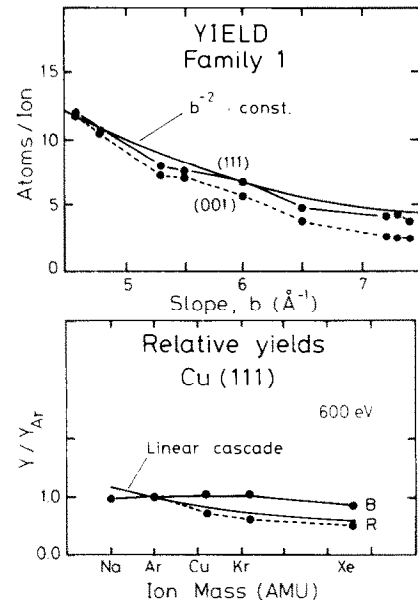


Fig. 2. Upper graph: Variation of Ar–Cu sputter yield with Born–Mayer screening radius b^{-1} for ion–target interaction. Full circles: Simulation [65]. Full drawn curve: Analytical result for $m = 0$ [47]. Lower graph: Relative sputter yield for copper versus ion mass at constant ion charge ($Z_1 = 18$) at $E = 600$ eV. Full circles: Simulation [66] for two Born–Mayer potentials B and R. Full drawn curve: Analytical result [47].

repulsive target–target interaction potential. It characterizes the stopping and scattering of target atoms at energies around the ejected energy ϵ , i.e., around U in case of the sputter yield. Undoubtedly, potentials from gas collisions can only serve for rough guidance, and the most reliable information can presumably be found by analysing suitable sputter experiments. For Born–Mayer interaction, one finds $m \approx 0.055$ [47]. This has been approximated by $m = 0$ in the most common version of eq. (3). The TRIM potential is roughly equivalent with $m = 1/6$ [44], and Lenz–Jensen interaction [54,55] with $m \approx 1/4$ at low energies. From the approximate $1/U$ dependence of the sputter yield on the sublimation energy [67,68], values of $m \geq 1/6$ would seem unrealistically high in view of eq. (3). This conclusion, however, depends on the adopted emission model, cf. sect. 2.2. A similar statement applies to energy spectra, cf. eq. (4), in view of the widespread acceptance of the ϵ^{-2} spectrum [8,69,70]. Also the few existing data on isotope effects in sputtering support the smaller $m \approx 0.055$, cf. section 5 and ref. [71]. The value $m \approx 0.2$ extracted from the same source in ref. [27] is due to an oversight [71]. However, the parameter m need not be the same for all target materials, and somewhat greater values [73] are to be expected for light elements [72], in view of the general scaling properties of screened-Coulomb cross sections [52].

It has been claimed recently, on the basis of simulations as well as analytical results, that the electronic energy loss of *moving target atoms* affects calculated sputter yields significantly [44,74,75]. These results hinge on the assumption of velocity-proportional electronic stopping [76,77] down to energies of a few eV. Since the target *nuclear* stopping power is proportional to ϵ^{1-2m} [5,42,52] electronic stopping dominates at low ϵ if $m < 1/4$. Evidently, the effect is more pronounced for Born–Mayer repulsion [74] where $m \approx 0.055$ than for $m \approx 1/6$ [44]. These results are formally correct and consistent with earlier work [78–80], but their significance rests on electronic stopping power expressions which are known to (only roughly) describe experiments at energies 3–4 orders of magnitude higher [81]. While an inelastic component is always to be expected, its magnitude is subject to considerable doubt at these low energies. Therefore, the present author is more worried about the validity of binary interaction potentials and binary collision dynamics than about electronic stopping at eV energies. After all, we know that eV collisions in gases have a dominating elastic component.

Attempts to improve eqs. (1)–(4) on the basis of analytic transport theory have concentrated mainly on light-ion sputtering as well as analysing the influence of a free surface.

In light-ion sputtering, due account needs to be made of sizable reflection coefficients, in particular for grazing incidence [82,83]. Measured energy spectra of

sputtered atoms [84,85] show pronounced peak shifts toward lower ejection energies at surprisingly high beam ion energies (e.g., 8 keV He⁺ on Zr). Existing attempts at a properly modified transport theory show the right trends but too little quantitative change [86,87].

Eqs. (1)–(4) have been derived on the basis of an infinite medium with a source of particles in a plane through which, for backward sputtering, also the flux of emitted target atoms is evaluated [47]. Replacing an infinite target by a semi-infinite medium has distinct effects with regard to the dependence on beam parameters on the one hand and target parameters on the other [5]. For physical insight, it is desirable to study the two effects separately.

Existing attempts are not specifically directed at one or the other [88–91]. Energy spectra are found to be insensitive to the introduction of a free surface [90]. Any pronounced difference found in other quantities [88,89,91] are subject to some doubt because of the use of hard-sphere interaction cross sections for analytical convenience. Such a collision spectrum enhances the frequency of wide-angle scattering events and hence the importance of multiple crossings of the reference plane in an infinite medium. Thus, what is gained on target geometry may be more than lost on the interaction cross section.

A successful yield calculation for normal incidence [93] has apparently never been generalized to the case of oblique incidence. It is, however, well established [92,44] that the surface exerts a major influence on the angular dependence of any emission yield at grazing incidence.

2.2. What about the model itself?

In ref. [47], the absolute agreement between eqs. (1)–(3) and existing experimental yield data was good within about a factor of 2, i.e., certainly better than the a priori accuracy of the theory which hinges on the model of low-energy atomic motion, of surface and bulk binding, and the ion–atom potential. Since there are systems where the agreement with experimental data is even better (cf. fig. 1), it appears both justified and desirable to test the underlying physics and to decide whether such agreement is fortuitous. I do not wish to give an answer, nor even indicate an opinion, but I want to mention a few central points and comment some discussion that has appeared in the literature.

I have often been asked about how many collisions there are required in a cascade for the linear Boltzmann equation to be valid. The straight-forward answer is, the fewer the better. The *statistical* accuracy of the equation is determined by the *number of bombarding ions*, and that is usually very large, except when field–ion-microscope images are analyzed. Thus, the passage of a particle beam through a thin layer is accurately described by Boltzmann’s equation, even in the extreme

case where only a small fraction of the beam particles collide [94,95]. The accuracy of the *linear* Boltzmann equation is limited toward *large* numbers of collisions, i.e., when nonlinearity becomes important, cf. section 3. One reason for mentioning this is a long series of false conclusions and implications drawn on the expectation in ref. [11] that some sort of equilibrium in a collision cascade is needed before Boltzmann's equation starts to be valid.

The above statement does obviously not contradict the fact that eqs. (1)–(4) are only valid in case of large enough ion energy and target thickness to allow a certain number of recoil atoms to be set in motion. But that is a matter of finding a simple *solution* to the transport equation.

Let us, then, look at characteristic depths in sputtering. According to ref. [47], there are two of the kind. The first is the depth of origin of the sputtered particles, given as $\Delta x = 5 \text{ \AA}$ which was a fairly small depth at the time, considering alternative approaches [96,97]. The second is the depth containing those collision events which eventually result in atom ejection, i.e., the minimum target thickness for the sputter yield to saturate. The latter, called x_0 , was found to be a sizeable fraction of the average damage depth (25–50%), except for light ions where it was found to be even larger. At high ion energy, x_0 is evidently much greater than Δx , a result that has recently been confirmed by MARLOWE simulations [98]. This also indicates that the claim put forward in ref. [11] that only collisions as deep as up to the fourth atomic layer lead to sputtering, can only be justified at low enough energies where ions do not penetrate much deeper. (Note, furthermore, that all molecular dynamics simulations summarized in ref. [11], with the exception of ref. [62], refer to bombardment along a main single crystal direction.)

The depth of origin of sputtered atoms has received considerable interest lately. In ref. [99], it was found to be distributed approximately exponentially, in agreement with results found from MARLOWE simulations [98,100] except for the scale. Molecular dynamics simulations showed emission almost exclusively from the topmost atomic layer, even at keV bombarding energies [11,101]. Both types of simulation work with perfect crystal lattice structures with intact surface planes. Monte Carlo simulations show sputtered atoms to come from greater depths [44,50], in good agreement with analytical estimates, keeping in mind the difference in the interaction potential. Experimental investigations on the basis of the temperature dependence of bombardment-induced composition changes in NiAu and NiCu alloys [102–104] have lead to the conclusion that *at least* 35% of the sputtered atoms must come from beneath the topmost layer. An opposite conclusion was reached for sputtering from a liquid GaIn eutectic where 85% of the atoms were quoted to originate in the

topmost layer [105]. An unexplained feature in the latter set of data is a drastic difference in the experimental data quoted for 15 keV and 25 keV Ar^+ bombardment, respectively: All available experimental and theoretical evidence would suggest differential quantities like sputter depth and angular spectrum (cf. below) to be rather insensitive to a variation of ion energy in that interval, for normal bombardment. Moreover, there is evidence for a surface impurity layer in the quoted ion scattering spectra [105,106]. Such layers have been shown [107–110] to drastically affect the angular spectrum of sputtered atoms, a key quantity in the analysis of ref. [105]. That experiment, beautiful and important as it appears, ought to be repeated in my opinion.

On the basis of the above evidence, as well as on further simulation results, it was concluded [111] that the mean depth of origin of sputtered atoms is 0.80 ± 0.10 mean atomic spacings, i.e., less than 2 \AA for many elemental targets. In view of the above reservations concerning the few available experimental data, and in particular in view of the discussion on surface segregation in section 5.2 below, I suggest that one take the quoted mean value with considerable caution and disregard the quoted error bounds.

Some implications may, however, be worthwhile to be pointed out if unequivocal evidence should show up in favor of sputter ejection near-exclusively from the top monolayer. In that case, the material parameter Λ in eq. (1), which contains a low-energy cross section $\propto C_m$ in the denominator, will instead be governed by a quantity characterizing the attenuation of energy from deeper layers which is rather insensitive to the interaction potential. The parameter m is going to drop out from the energy spectrum, eq. (4), the isotope effect is going to be halved, i.e., $\propto (M_j/M_i)^m$, cf. ref. [71], and the dependence of the yield on surface binding is going to be $\propto U^{-1}$.

In this context, a few more remarks on angular distributions of sputtered atoms may be appropriate.

Eq. (4) predicts a simple cosine law, a result that is rarely found experimentally. Apart from the impurity effect [108–110] there are several factors that affect the angular spectrum. At low ion energy, the collision cascade becomes more or less anisotropic. The transition has been traced by Monte Carlo simulation [44]. Early analytical estimates [112–114] give the wrong sign of the anisotropy, because of ignoring the variation with depth of the deposited momentum [115,116]. Caution is indicated with regard to subsequent work [117] because of the use of an arbitrary, undefined, and irrelevant energy parameter E_1 in the analysis [118].

At moderately high ion energy above a few keV, anisotropy should be unimportant, and the angular spectrum should be independent of the ion energy. Most existing experimental data indicate spectra that are narrower than the cosine law eq. (4) in the medium

and upper keV range [119–122]. The fact that they are narrower appears less serious than that they may also depend on ion energy [122]. An apparent broadening at the highest energies [122] needs additional measurements.

Among the factors affecting the cosine law is a depth-dependent source strength [108]. In ref. [99], the recoil density was assumed depth-independent, an assumption that is sensitive to the infinite-medium approximation. It has been shown recently [123] that the correlation between angular spectrum and depth of origin survives inclusion of scattering into the model, a point ignored in ref. [111]. Also, an atom passing a surface at an oblique direction suffers a net deflection toward the surface normal because of lacking azimuthal symmetry of the location of scattering centers (fig. 3). A rough small-angle evaluation of the latter effect, assuming a random distribution of scattering centers, indicates that this effect alone can transform the spectrum into $(\cos \phi)^\beta$ shape with $\beta \approx 1 + (8/3)NC_0^{3/2}$, where C_0 is the constant C_m in eq. (2) for $m = 0$. With the parameters adopted in ref. [47], this yields $\beta \approx 1.55$, i.e., an effect of sizeable magnitude. This effect is evidently incorporated in computer simulation models that operate with an initial target configuration [11,45]. In Monte Carlo simulations, one has the option to include it or not, dependent on the adopted surface model. The effect is presumably included in the TRIM-SP code [44], and the resulting angular spectra are indeed narrowed, although the reason has not been specified. The effect is not included in the planar-geometry version of the Boltzmann equation [5,88–91], whatever the infinite or semi-infinite medium is analyzed.

The surface binding model, a crucial ingredient in all modelling of sputter processes, has received attention in several contexts. In most binary collision simulations and analytical models, surface binding needs to be

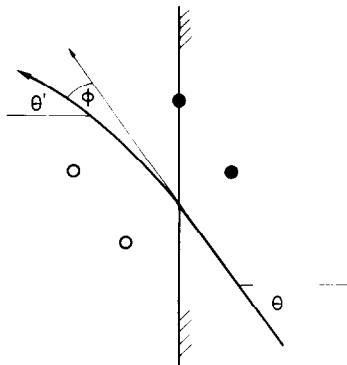


Fig. 3. Narrowing of the angular spectrum of sputtered particles by “missing atoms”. During passage through the surface at an angle θ , an atom sees an asymmetric distribution of atoms, and therefore experiences a mean deflection ϕ toward the surface normal.

superimposed as a separate item, in addition to target structure, bulk binding energies, and collision dynamics. A planar barrier is the preferred choice, not the least because there has never been pointed at an alternative explanation for the experimentally observed maximum of the energy spectrum of sputtered particles [48], the position of which depends on the target material but not on ion energy except under spike conditions or near threshold [4,8,69,70]. In molecular dynamics simulations, the matter is complicated due to the fact that the adopted binary target–target potential, tailored to generate a stable crystal, generates an effective surface barrier which may or may not warrant the introduction of additional surface forces in order to generate a realistic effective surface barrier.

It has been mentioned [33] that a systematic comparison of simulation results found by different simulation models, desirable as it may be [124,125], is hampered severely by difficulties in generating equivalent surface binding conditions.

The actual value of the surface binding energy has been taken up repeatedly in connection with the sputtering of alloys and compounds [27,126], and in a recent, rather detailed analysis of available thermodynamic and other data [127]. The main drawback of the latter treatment, although useful and informative, is the uncritical use of a planar surface barrier in the analysis of experimental yields and energy spectra. While a planar barrier emerges readily from a model in which the cohesive energy is an electron gas property, its validity is by no means ensured in the case of site-dependent surface binding in terms of atom–atom bond strengths [128].

2.3. Single crystal sputtering

Single crystal sputtering phenomena are receiving interest again. Evidently, much computer simulation work has always been done on crystal lattice models, and many experiments were carried out on crystals, but for a long period the main attention was paid to phenomena that were thought to be insensitive to lattice structure and orientation.

On the experimental side, interesting developments include the application of the field-ion microscope [129], atom diffraction [130], and two-photon laser spectroscopy [131] along with more conventional techniques [8,132].

On the theoretical side, computational studies have been devoted to the relative significance of directional and random processes in single crystal sputtering [133,134]. The possibility has been explored [135,136] to determine adsorbate positions from sputter desorption patterns, a technique well-established in electron-stimulated desorption [137]. Mention may be made of studies to identify systematic differences between polycrystalline and random target behaviour in sputtering [138,139].

3. Dense cascades (spikes)

Experimentally one finds that eq. (1) underestimates the sputter yield in case of very-heavy-ion bombardment of heavy target materials over a broad energy range around the maximum [1,5,40,47,140]. It is reasonably certain that this discrepancy is not caused by an error in the adopted ion-atom potential function.

Another finding is yield enhancement for heavy molecular-ion bombardment (Te_2^+ , Sb_2^+ , Sb_3^+ , etc.) which has been measured to easily amount to more than a factor of 2, and up to almost an order of magnitude [142,143].

Pronounced low-energy peaks have been found in the energy spectra of sputtered particles in case of heavy-particle bombardment [144,145,8]. These peaks have been analyzed in terms of evaporation from localized heated regions around the point of ion impact.

Unfortunately, no experimental results seem to be available on energy spectra of sputtered particles for molecular-ion impact in comparison with atomic ion bombardment at similar speed.

Finally, pronounced surface craters have been shown to form during bombardment with heavy ions and molecules [146,147].

Crater formation, molecular enhancement, and high sputter yields demonstrate most clearly that a basic assumption underlying linear cascade theory and Monte Carlo simulation codes, that of low density of moving atoms, cannot be fulfilled under bombardment conditions involving a high density of energy deposition.

This limitation was expected on theoretical grounds, and various implications were mentioned long before the above experiments were performed [148–150]. The experiments described in ref. [142] were specially directed at separating high-density effects from the influence of the ion-atom potential. The observed magnitude of the molecular-enhancement effect, however, was beyond expectation.

It is interesting to note that these phenomena have received almost no attention from the computer simulation community. In Monte Carlo simulation studies, high-density phenomena may easily be overlooked, unless explicit attention is given to the number of recoil atoms within a given target volume. However, the Au–Au system has been investigated, and the results confirm the conclusion that a major fraction of the target atoms is set in motion, as well as that the simulated sputter yield is less than measured [141]. A simulation of nonlinear cascades requires keeping track of the time sequence of collision events, a feature that is (although need to be) absent in many simulation codes except molecular dynamics codes. The latter, on the other hand, may be hard to apply in the range of energies where pronounced nonlinear effects have been found because of limitations in computational capacity.

Spike phenomena have been considered long ago [151,152], mostly as alternative (and simpler) descriptions of radiation effects due to energetic particle bombardment. The present spike concept (called energy spike, elastic-collision spike, or alike) is connected to a high deposited energy per cascade volume, the mean energy per atom approaching the critical energy for defect formation, sputtering, etc. [1,41,153–155]. Since the expected common reason for the observed phenomena is the breakdown of the linear Boltzmann equation, i.e., an equation that does not obey particle conservation, it would seem logical to go back to the nonlinear Boltzmann equation which does conserve particle number, *all other parameters like potentials and binding energies remaining the same*. While an ab initio solution of the full nonlinear Boltzmann equation under conditions applying to particle bombardment has never been performed to the author's knowledge, it is well known that continuum theories of heat conduction and shockwave propagation can be based on the Boltzmann equation. Therefore, material parameters like heat conductivity can be based on parameters governing collision processes in the energy range in question [41]. Such a procedure is to be preferred to the use of macroscopic material parameters that are measured under quite different conditions.

3.1. Shockwave model

Most investigators adopted the physical model of a linear collision cascade ending up in a thermal pulse [156] of high temperature, several thousand degrees [1,41,157,158], while others assumed shockwave propagation [159–161]. With regard to the latter, the original suggestion [159] was understood as if atomic motion in the primary collision cascade were sufficiently coherent to be describable in terms of shockwaves. Although that was unintentional [162], it was shown that such coherent motion in a single cascade could not arise under conditions of keV heavy-ion bombardment [163], a conclusion that appears consistent with simulation results [164], although the latter authors seemed to advocate the opposite conclusion from their results by considering the average motion of an ensemble of cascades.

My main objection against a shockwave picture of the *primary* cascade is the fact that it is bound to move *inward*, i.e., it will not cause sputtering, even if a pronounced shockwave exists. This, of course, does not preclude a secondary shockwave to propagate from the center of the collision cascade, i.e., the top of the deposited-energy distribution (fig. 4). Although the momentum distribution of such a system contains a net component directed away from the cascade center [115,164], that component has been found to be quite small in comparison with the random one [165].

Existing evaluations of nonlinear sputter yields based

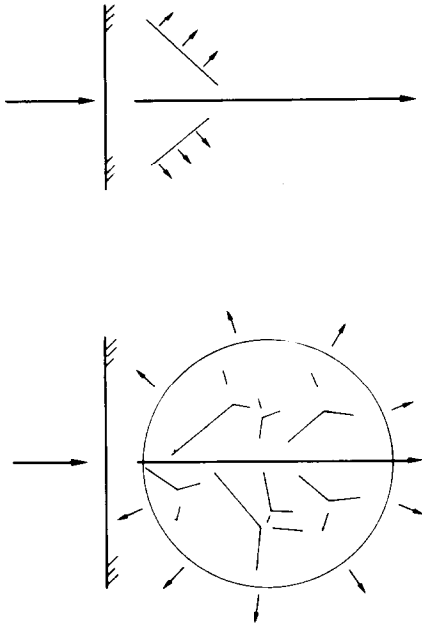


Fig. 4. Propagation of energy in a dense cascade. Upper graph: "Primary" shockwave. Lower graph: "Thermal" pulse or "secondary" shockwave. See text.

on the shockwave model [161,166,167] utilize macroscopic or phenomenological parameters. The relation to the linear cascade is, therefore, not clear at all. At least in one case [161], the seemingly good agreement with molecular-ion yields has been achieved by applying fitting parameters [168] which, for atomic bombardment, are clearly unphysical.

The present consensus [162] appears to be that there must be some degree of coherent motion in a collision cascade which, however, most likely does not explain the main part of nonlinear sputtering yet might well play a role in other phenomena like ion-induced changes in surface morphology, a topic that has been left out in this survey.

3.2. Heated zone model

While the very concept of a heated zone dates back to the beginning of this century [169], its physical significance has never been universally accepted because of the obvious objection that both the size and the duration of a collision-induced spike may be too small to allow for the establishment of some sort of thermal equilibrium. However, there has come up increasing theoretical evidence that the energy distribution of target atoms comes close to Maxwellian shape within the characteristic time span of less than $\sim 10^{-11}$ s which is typical for an elastic-collision spike [170–173]. This

does not preclude the coexistence of rather different pictures of the underlying physical mechanism [41,174], but indicates at least that Maxwellian portions, identified in numerous measurements of sputtered-particle spectra [8,144,155] may indeed be related with the establishment of local equilibrium in the kinetic energy of target atoms. Estimates of sputter yields and energy spectra based on this model have been based either on material parameters consistent with the adopted interatomic potential [41,158,175,176] or on macroscopic thermodynamic parameters [157,178,179]. The geometric shape of the spike was usually oversimplified, being taken cylindrical [175], spherical [176,177,180], or at least ellipsoidal [157].

The thermal conductivity was taken either independent of temperature [157] or a power law [41,175,176, 180–182]. The difference has been shown to be unimportant [182]. A simple cylindrical spike model with reasonable input regarding primary energy deposition and planar surface binding as in linear cascade theory has been shown to yield qualitative agreement with observed yield enhancements [175], even in case of very drastic enhancement [143,179]. The neglect of heat loss by evaporation in that calculation has been justified in subsequent work [183].

Despite this qualitative success, the physical picture is by no means generally accepted [31,154,178]. Here are some of the points that have been raised in the discussion. Until a few years ago, sputter yield enhancements measured on many targets at high temperatures [184] were often claimed to provide evidence for the existence of hot spikes [8]. When it turned out that the experimental results could not be reproduced under ultrahigh vacuum conditions, it was first concluded [185] that the new finding removed an essential basis for the existence of hot spikes. Recent experimental work [186] showed, on the contrary, a pronounced temperature dependence of the sputter yield under conditions of low energy deposition (25 keV helium on molybdenum). Subsequent discussion [182,187] made it clear that the logical connection of such a phenomenon to spikes was not justified, first of all because spike temperatures in question were so high (many thousand degrees) that an increase in target temperature of a few hundred degrees would not substantially affect evaporation rates from spikes [182]. Although the point had been made rapidly, it came too late to prevent the original news from spreading into the review literature [12]. The hot-spike picture was strongly promoted in ref. [157] where it was argued that spike parameters need to be based on the collision theory of energy deposition [150]. In subsequent work, the same author not only abandoned this viewpoint but also denied the importance of evaporation from heated spikes [178]. The latter conclusion was based on the adoption of (much lower) spike temperatures extracted from measurements of charge and exci-

tation states of sputtered particles, analyzed by means of the so-called LTE model [188] which implies an accompanying high *electron temperature* and, not the least on grounds of discussion in this series of workshops, has been replaced by alternative and much refined models [36,37].

3.3. Crater effects

It has been pointed out by several authors [154, 179,183,189] that the high sputter yields observed under spike conditions must lead to crater formation, in agreement with experimental observations [146,147]. Therefore, sputter yield calculations need to consider the effect of surface recession *during* the duration of the cascade, as well as a modification of the effective barrier potential. It was asserted [179,189] that these effects would explain observed yield enhancements within the framework of linear cascade theory without invoking a nonlinearity in the collision cascade. While both effects are undoubtedly noticeable, they certainly do not account for order-of-magnitude yield enhancements [183]. More important, refs. [179,189] overlooked the point that crater formation by itself is a sufficient criterion for the cascade to be nonlinear. Therefore, crater formation is an effect that needs to be considered in spike phenomena, but only in conjunction with a model for nonlinear cascades, not instead of it.

3.4. Conclusions

With regard to the sputtering of metals and semiconductors under high density of energy deposition, I find that the physical model invoking evaporation from heated spikes has not really developed to a quantitative theory but I cannot see an alternative model that would be equally or better justified.

A case of particular current interest is the bombardment of condensed noble gases with heavy ions in the lower keV region. Sputter yields can be very high, as much as several thousand atom per ion [190–193]. This, as well as the related fact that surface binding energies lie in the MeV range, suggests considerable caution with regard to linear cascade theory as a valid tool in the interpretation. Nevertheless, some success has been achieved in this connection [191]. The straight cylindrical-spike model has been applied equally successfully [192], despite some warnings expressed in ref. [183].

With the low surface binding energies in question, the density of energy deposition may easily get so high that there is no effective surface barrier. Under these conditions, existing spike models break down [175,183], and a gasflow model may become more appropriate [194]. While, even within a physical model of noble-gas sputtering by elastic collisions, there is a considerable uncertainty with regard to the importance of the perti-

nent processes, the role of electronic excitation is by no means clear. While it is well established that under conditions of dominating electronic stopping, i.e., for high-speed particle bombardment, sputtering must be due to electronic processes, the opposite conclusion is not necessarily true under conditions of dominating nuclear stopping, in view of the fact that electronic stopping dominates much more strongly at high projectile speed than nuclear stopping does at low projectile speed. Little is known about the efficiency of conversion of electronic excitation at low projectile speed into particle emission.

4. Sputtering of molecules

The first theoretical attempts to understand the sputtering of small molecules and clusters date back to about a decade ago [195–197]. Progress in the theory can be inspected from several recent reviews [198–201]. Only selected aspects of molecule emission have been investigated theoretically, as is evident from the experimental literature on molecule and cluster emission [18,23–25,202]. In accordance with what was said in the introduction, the present comments will be quite brief.

Least is known theoretically about the sputtering of large clusters and molecules. In fact, there is no firm evidence to support the rather common assumption that in the nuclear stopping regime, i.e., for keV heavy ion bombardment, large-molecule emission should be initiated by elastic collision events. The similarity of measured mass spectra to those found under conditions of sputtering by electronic excitation [17,203] lends support to, yet does not prove by any means, the opposite assertion.

Experiments with molecular beams may throw light on the question. For keV heavy molecular ion bombardment, a pronounced nonlinearity should be achievable with regard to the nuclear energy deposition, in particular in targets like CsI which, to the sputterers' surprise, is considered to be the standard model biomolecule by the mass spectrometry community [23,204]. Conversely, bombardment conditions may be chosen at the same time to ensure that the electronic energy deposition should be close to linear.

A reliable answer to the above question is desirable in particular in view of the fact that with the exception of a single high-energy experiment [205], experimental results on large-molecule emission refer to the *ionic* component of the emitted flux which, even for bio-organic substances, has been demonstrated [205] to constitute only a very minor fraction of the total emitted particle flux.

More advanced is the modelling of small-molecule emission. Early investigations [195–197,206,207] focused on what was called a recombination mechanism, i.e.,

molecule formation in front of the target surface by particles ejected as atoms, the criterion being that the relative kinetic energy of any two or more ejected particles would be less than their attractive potential energy. An alternative process is the direct emission of a preformed molecule present in the solid. Whether or not these models are essentially different from each other depends on several factors such as the role of long-range interactions in the target and the model adopted for surface binding. The role of inelastic processes for molecule formation by recombination, while well-known in gas chemistry for a long time, was explored only more recently [208,209]. At the same time, optical spectroscopy was explored as a tool to study molecule sputtering in detail [2,10,211,213].

Modelling recombination processes is furthermore complicated by the fact that atomic particles are emitted in a variety of electronic states.

Taking into consideration the complexity of the processes involved, no more than a very qualitative understanding of molecule sputtering can be expected, such as the non-Boltzmann nature of observed rotational and vibrational spectra [209,211,212] which, however, is not universally accepted [213,214].

Feasible estimates have been done mostly on the ejection of sputtered adsorbates [199,212,215,216] where there is little doubt about the direct emission of pre-existing molecules, whether knocked off by the collision with one or more of the constituents of the molecule.

5. Sputtering of multicomponent materials

This section deals with the sputtering of alloys and compounds. The topic has been studied intensely during the past ten years [26,27,217–221] motivated mostly by its crucial importance in surface analysis and thin film technology. While it was obvious long ago that sputtering studies on truly elemental targets are the exception rather than the rule, it became increasingly evident that sputtering experiments on multicomponent targets may elucidate fundamental aspects of the sputter process that are difficult to identify on elemental targets.

Experimental work may be divided up into measurement of bombardment-induced composition changes in the target by Rutherford backscattering, Auger electron spectroscopy, and low-energy ion scattering in the depth ranges of 10^2 , 10^1 , and 10^0 Å, respectively, and measurements of the sputtered flux by collection or by laser spectroscopy.

It may be instructive to introduce this section with a historical remark. In 1891, W. Crookes mounted a cathode of gold–aluminium alloy into a discharge tube. After exposure, the electrical action was found to have changed the original purple appearance of the alloy “to the dull white colour of aluminium”. Crookes’ conclu-

sion was that “the gold is first to volatilize under electrical influence, the aluminium being left behind” [222].

The main message from this experiment is that ion bombardment must have produced changes in alloy composition that were visible even to the naked eye. Whatever the cause, it cannot be sputtering alone, because the depth range affected by sputter erosion is far below that resolution.

A second observation is the fact that Crookes’ result apparently contradicts modern measurements that show enrichment of gold rather than aluminium, both by Auger spectroscopy and Rutherford scattering [223,224], at least at room temperature. Discrepancies of this kind, real or by artefact, are not uncommon.

Fig. 5 shows composition profiles of PtSi measured by Rutherford backscattering after argon bombardment [225]. It is evident that pronounced deviations from bulk composition occur near the surface, about a factor of two, and that the thickness of the altered layer increases with increasing ion energy, i.e., with increasing penetration depth of the beam.

At least three different mechanisms have been proposed during the past decade to explain observations of the type of those shown in fig. 5.

(I) Silicon is sputtered preferentially, i.e., the ratio of sputter yields $Y_{\text{Si}}/Y_{\text{Pt}}$ is higher than the ratio of atom fractions within the depth of origin of sputtered par-

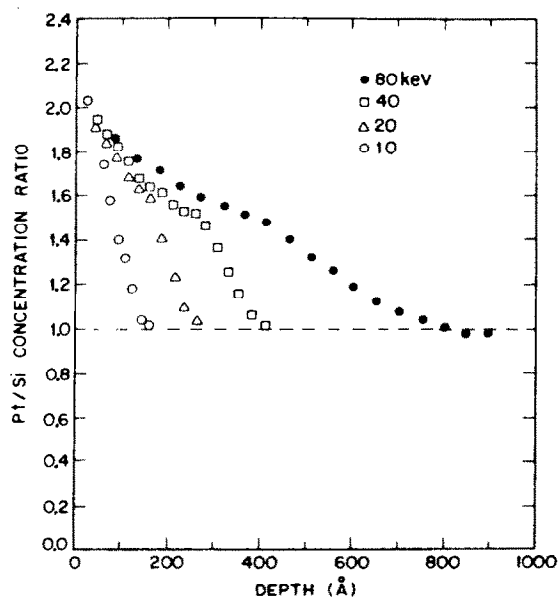


Fig. 5. Concentration profile of an initially homogeneous PtSi alloy after argon bombardment of energy 10–80 keV. From ref. [225] by courtesy of the authors and The American Institute of Physics.

ticles. Some efficient transport process compensates the resulting strong composition gradient by supplying silicon atoms to the surface layers from the entire damaged region.

If the data in fig. 5 are to be explained by this mechanism, sputtering must be strongly preferential in PtSi, by at least a factor of two, and transport of matter must be sufficiently rapid to beat the sputter process.

(II) Silicon segregates at the surface and is removed from there by sputtering. This implies that the composition ratio in fig. 5 changes sign in the very surface region, but such a change would be below the resolution of Rutherford backscattering.

This process does not require the sputter process to be preferential. It does, however, require an efficient mechanism for transport of matter to the uppermost surface layer(s).

(III) A profile like the one shown in fig. 5 has little to do with sputtering but represents the near-surface portion of a recoil implant profile. This implies that at greater depths, the target must be silicon-enriched.

It is reasonably certain that each of the three mechanisms has a certain range of validity in terms of target materials and bombardment conditions. The theory of process I has been reasonably well developed in a phenomenological sense [226–242], i.e., with adaptable parameters characterizing diffusion and preferential sputtering.

The significance of process II has been recognized slowly, by systematic analysis of apparent discrepancies between Auger and ion scattering signals with respect to the sign and magnitude of observed composition changes [27,107,243], from pronounced composition gradients showing up in angular spectra of sputtered atoms [122,244–246], from sputter measurements at elevated temperatures [102,103,247–249], from atom-probe field ion microscopy [251], and from more general observations [250].

Process III, although originally discussed [252] in connection with fig. 5, is most efficient at much lower energies, near the sputter threshold [71].

Evidently, effects II and III are driven by processes other than sputtering [253–257]. On the other hand, in both cases, pronounced composition gradients may be generated near the surface which may influence the sputter process and thus give information on central issues in sputtering (see below). Conversely, process I is driven by preferential sputtering and is, therefore, an issue more closely related to the present survey, although possibly less important as a whole.

As a general rule, preferential sputtering, segregation, and collisional mixing all work strongly against a straight “layer by layer” sputtering model [258]. This, however does not necessarily prevent specific materials from keeping or, more likely, continuously restoring their stoichiometry during ion bombardment [26].

5.1. Preferential sputtering

Preferential sputtering is most pronounced at bombardment near the sputter threshold [259–264]. For a system like tantalum oxide bombarded with helium, at low enough energy virtually no tantalum atoms can be knocked out while the energy transfer to oxygen atoms may still be very efficient. Hence, very pronounced composition changes occur that are readily explained by standard collision theory [264].

At higher energies, in the linear cascade regime, mass effects are predicted to be much weaker. For a homogeneous target, i.e., for low fluence, the following relation has been derived [5,71,72] for the sputter yield ratio Y_i/Y_j of two components i, j in a random alloy:

$$\frac{Y_i}{Y_j} = \frac{\alpha_i}{\alpha_j} \left(\frac{M_j}{M_i} \right)^{2m} \left(\frac{U_j}{U_i} \right)^{1-2m}, \quad (5)$$

where α_i , M_i , and U_i are the atom fraction, mass, and surface binding energy of atom i , respectively. Evidently, the mass effect is weak for $m = 0.055$ but quite noticeable for other advocated choices of m : For $m = 0.18$ [44], the mass effect alone could account for the factor of two change seen in fig. 5, in qualitative agreement with the results of simulation work [265].

Alternative theoretical estimates of preferential sputtering yielded larger [266,267] or smaller [268,269] effects than those predicted by eq. (5). Clear preferential sputtering effects have shown up in Monte Carlo simulation work [265,270–272], as well as by molecular dynamics simulation of *ordered* alloys [273]. The particular case of preferential sputtering of isotopes [265,268,269,274] has been discussed in great detail [71], and on that occasion the author finally succeeded to find a transparent way to show the physical origin of the mass dependent factor in eq. (5).

Another possible cause of preferential sputtering emerges from fig. 3. Evidently, the deflection angle ϕ depends on the sputtered species. For a planar surface barrier, the sputter yield increases with increasing ϕ , i.e., increasingly normal ejection. For an isotopic system, this leads to preferential ejection of the light isotope, i.e. an effect going in the same direction as eq. (5).

The limitations of a model of alloy sputtering based on the process labelled I above have been summarized repeatedly [275,276].

5.2. Surface segregation

With regard to process II, a systematic comparison between thermodynamic data and measured composition changes appears to demonstrate the importance of Gibbsian adsorption in sputtering experiments, also at temperatures where the pertinent transport processes would be frozen out in the absence of ion bombardment [253].

While I do not feel qualified to add anything substantial to recent summaries on radiation-induced Gibbsian segregation [253,254], I do wish to make a couple of general remarks.

The first one concerns the wording. By and large, we all had to realize, sooner or later, that bombardment-induced composition changes may have very little to do with sputtering. It is, therefore, puzzling that some of those whose work more than that of others stimulated that change, keep on using terms like “sputter-induced” instead of “bombardment-induced” composition changes [247,248] or the role of Gibbsian segregation on “preferential sputtering” instead of “surface composition” or “sputtered flux” [253,257].

The second remark concerns the phenomenological description of sputtering and matter transport in the presence of Gibbsian segregation, i.e., a pronounced composition gradient at the surface. Most existing theory implies slowly varying composition profiles [26,27,226–238,240–242] where the partial sputter yields are taken proportional to the respective surface concentrations. In a situation where the composition profile may vary drastically over the depth of origin of sputtered atoms, such a description is totally inadequate. This inadequacy showed up in the analysis of the measurements in refs. [102,103].

A more adequate scheme was proposed in ref. [108] where the partial sputter yield was set equal to

$$Y_i = \int_0^\infty dx N_i(x) \sigma_i(x) \quad (6)$$

for a target with a plane surface at $x = 0$. Here, $N_i(x)$ is the mean number of i -atoms per volume at depth x and $\sigma_i(x)$ is a depth-dependent ejection function which, to some extent, depends on the environment, i.e., the composition of the target down to and somewhat beyond depth x . Since $\sigma_i(x)$ has the dimension of an area, it may be called a sputter cross section. *Unless*

$$\sigma_i(x) = \sigma_j(x) \quad \text{for all } x \text{ and all } i, j, \quad (7)$$

sputtering is preferential

Evidently, if $N_i(x)$ varies slowly over the depth range over which $\sigma_i(x)$ is nonzero, eq. (6) reduces to

$$Y_i \approx N_i(0) \int_0^\infty dx \sigma_i(x), \quad (8)$$

which is the relation underlying the phenomenological theories of preferential sputtering. When eq. (8) breaks down because of a pronounced composition gradient, also the concept of a “component yield” [26], i.e., $N^{-1} \int_0^\infty dx \sigma_i(x)$ in the notation of eq. (8), with N the overall number density, loses its value, as well as the commonly used definition of preferential sputtering [27], i.e.

$$Y_i/Y_j \neq C_i(0)/C_j(0), \quad (9)$$

where $C_i = N_i/N$. The latter fact is less severe than one

might have thought since, in view of eq. (7), sputtering is *a priori* preferential.

In passing on, I should like to reiterate the point [108] that the popular term of a “total sputter yield” of an alloy, i.e., the quantity $Y = \sum_i Y_i$, is of no use whatsoever and should be abandoned. There exists no technique to measure Y directly, i.e., by counting *atoms* regardless of species and state of aggregation; in fact, any technique that determines Y requires measuring all Y_i separately, either directly or indirectly. An equivalent statement holds for theoretical determinations, unless the difference between different species may be ignored altogether, as is most often done for isotopic differences.

Fig. 6 shows a schematic view of the composition profile of an alloy in the presence of radiation-induced Gibbsian segregation. Only high-fluence profiles have been plotted, i.e., it is assumed that the composition of the sputtered flux is equal to the bulk composition. Preferential sputtering has been assumed insignificant. The upper graph indicates the case where the depth of origin of sputtered particles is within the thickness of the segregation layer, e.g., both being one monolayer thick. The lower graph shows the corresponding profile under the assumption that also particles from beneath the segregation layer contribute noticeably to the sputtered flux. Evidently, the requirement that the sputtered flux has bulk composition then raises the near-surface portion of the profile. A similar profile would appear if B were sputtered preferentially. Thus, an increase in the depth of origin of sputtered atoms may easily be misinterpreted as a consequence of preferential sputtering, and vice versa.

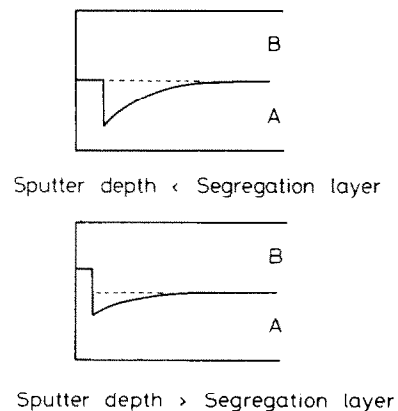


Fig. 6. Schematic view of the high-fluence depth profile of an initially homogeneous AB alloy. Preferential sputtering has been ignored. Component A is assumed to form a Gibbsian adsorption layer which may be either thicker (upper graph) or thinner (lower graph) than the depth of origin of sputtered atoms.

It is thus evident that a proper description of sputtering in the presence of segregation layers needs to be based on a relation equivalent to eq. (6) [108,277,239]. One may note that the formalism developed in ref. [242], although nominally based on ref. [108], does not satisfy this requirement since spatial variations like the one expressed by eq. (6) were excluded at an early stage.

The fact that measured angular dependences of the composition of the sputtered flux [122,244] were and are taken as evidence in favour of a segregation layer [111,253] implies that it is the lower graph in fig. 6 that applies to the materials investigated, i.e., that the depth of origin of sputtered atoms exceeds the thickness of the segregation layer. While this is in obvious contradiction with the main conclusion in ref. [111] regarding the depth of origin of sputtered atoms, the matter may well be complicated due to the surface scattering effect shown in fig. 3 which also contributes to a selective emission pattern. For an isotopic system, it predicts a narrowing of the angular spectrum of the lighter species. It is possible that this effect has been observed in ref. [274]. A detailed study is in progress.

5.3. Recoil implantation

Recoil implantation has been discussed occasionally in connection with sputtering [27,252,278,279]. Since it is a process involving direct ion-atom collisions, i.e., relatively rare events, it is important in situations where either the comparatively large implant depth is significant, or where the ion energy is so low that collision cascades involve only very few atoms. The latter case has been discussed [71] briefly in connection with isotope effects in sputtering [260]. A quantitative treatment is in preparation [280].

Fig. 7 shows the simultaneous action of preferential sputtering and recoil implantation in the absence of segregation [108]. An initially homogeneous A_xB_{1-x} alloy (a) experiences sputter-dilution in *both* components within a shallow surface area, and atom transport into deeper layers by recoil implantation (b). The magnitude and characteristic depth of either process differs for the two species. The configuration (b) is mechanically unstable and must relax, e.g. homogeneously, to a stable configuration (c). As a result, one finds a composition gradient near the surface which may predominantly be caused by preferential sputtering, and a layer of altered composition extending throughout the average damage depth.

An interesting controversy has arisen some time ago with regard to the sign of preferential recoil implantation. According to a simple rule of thumb, the lighter component in a binary material is recoil-implanted preferentially [252,281], a result that appears to be consistent with some computer simulations [282], and opposite to the result of others [270,283,284]. A closer look

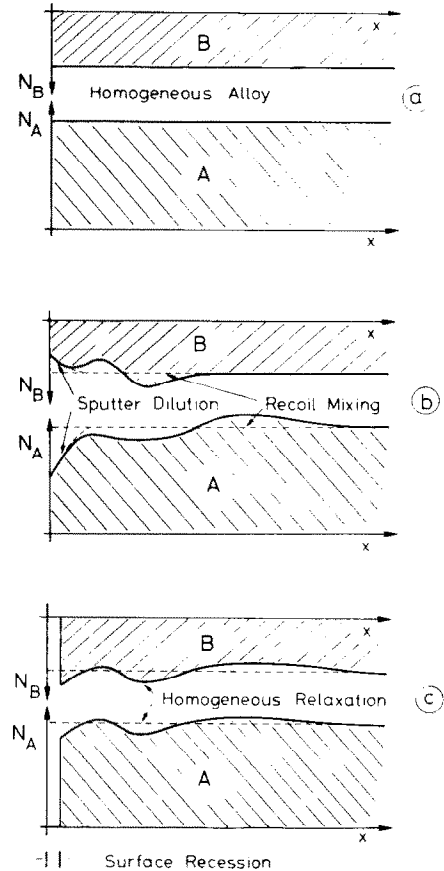


Fig. 7. Schematic view of the simultaneous effect of preferential sputtering, recoil implantation, and homogeneous relaxation. See text. From ref. [108], by courtesy of North Holland Publishing Company.

reveals that atomic numbers and masses enter in a variety of ways through the ion-atom collision cross section, the maximum energy transfer, the travelled path length of the recoiling atoms and their projected-range correction due to scattering. The latter factor, which is rather unimportant at high energies (medium and upper keV) is crucial at low energies, and it causes recoil ranges to increase with increasing ion mass. Its relative significance is easily seen to depend on the interatomic potentials involved. In consideration of this, as well as the fact that the effects of varying atomic number and mass, respectively, tend to cancel with respect to some quantities and add up with respect to others, the topic is just about complex enough to deserve a separate treatment which I hope to provide before long. It is remarkable, however, that two computer codes which are supposed to simulate the same physical situation make predictions of close to identical magnitude but opposite sign [284].

5.4. Final comments

As was mentioned already in the introduction to this section, general criteria are missing at the present stage that would allow predictions concerning the relative importance of Gibbsian segregation and preferential sputtering in generating composition changes at low and moderately high temperatures. An important piece of input is the possible mechanism of transport of matter either to support the segregation layer or to compensate for the effect of preferential sputtering. There is ample evidence from experimental work on ion beam mixing [234,285–288] to demonstrate that an ion bombarded layer can experience thorough intermixing at a fluence much lower than that necessary to remove one altered layer by sputtering. Mixing mechanisms have been the subject of extensive discussion [289–298] but no coherent picture has yet emerged. Although the topic is highly relevant to alloy sputtering, it is a bit too complex to be incorporated here in any detail.

6. Electronic sputtering

The topic of sputtering by electronic processes is undoubtedly the one where the most dramatic discoveries have been made during the past decade. Despite this, I shall refrain from a review at this stage, mostly since a great number of recent summaries are available [14–19,21,32,299–303]. As in section 4, I only wish to make a few scattered comments.

Electronic sputtering has been observed on a wide variety of insulating targets such as alkali halides, other luminescent materials, condensed gases, organic compounds, and large biomolecules. Bombarding particles may range from low energy (~ 10 eV) electrons and photons to GeV ions. Except in the case of keV heavy-ion bombardment (cf. section 4) there is usually little doubt about whether electronic sputtering dominates in a given experimental situation, the main criterion being the energy dependence of the measured yield which peaks at a much higher projectile energy than in case of knockon sputtering. This, however, does not imply that the series of processes leading from electronic excitation to emission of atoms or molecules is easy to trace, as is evident from the large number of proposed models [304–328]. At present, it seems unlikely that some universal mechanism is responsible for electronic sputtering in all materials.

Firm evidence is available in the case of sputtering of condensed noble gases by light ions and electrons [15,16,301] and a few similar systems [15,16] and, quite clearly, alkali halides [340], all showing a close connection between electronic sputtering and luminescent properties of these materials. In other cases, proposed models, interesting and stimulating as they may be,

have been difficult to reject or confirm.

With the exception of the alkali halide work, the development until quite recently was governed by a fairly general observation that electronic sputtering effects were essentially nonlinear [32,319]. This was encouraged by an early theoretical prediction [318], by the apparent lack of a sputtering effect in water ice under electron bombardment [319], and the rather general experience of very large sputter yields, while predictions and evidence to the contrary were overlooked [305,307]. Evidence for a linear regime came only gradually [320,321], along with feasible theoretical models [322,323] that tied the ejection of neutral particles to the decay of bombardment-induced excitons [305].

Another important step dealt with the interpretation of the observed variation of the sputter yield on target thickness and substrate material [190,329]. Initially, such an effect was ascribed to heat conduction in a thin layer via a thermal spike model [190], i.e., a nonlinear effect. Subsequently, it was shown that the observed dependence could be ascribed to exciton diffusion [323]. The two effects are easily distinguished; in a thermal spike theory, the critical thickness has the form [330]

$$L = \text{const } (Q/U)^{1/2}, \quad (10)$$

where Q is the deposited heat per unit length and U is the surface barrier. Evidently, Q is (not necessarily linearly [32]) related to the electronic stopping power. For a variation over an order of magnitude in the latter, the critical thickness was found to be essentially the same in case of solid argon bombarded by protons and alpha particles [321]. Hence, at least in that material, the thickness dependence of the sputter yield cannot be ascribed to thermal conduction.

The significance of exciton diffusion over several hundred ångström [323] provides a plausible explanation for the fact that electronic sputtering phenomena may be linear up to substantially larger sputter yields than in case of knockon sputtering. Exciton diffusion simply dilutes the pertinent cascade volume and surface area [302]. On the other hand, nonlinearities at higher excitation densities (up to several keV/Å) may arise both due to electronic effects (exciton–exciton interaction) and due to the overlap of “mini-cascades” [331,332] generated by different excitons, and may therefore be more complex in nature.

While there has thus been established a basis for detailed discussion of the electronic sputtering of condensed gases, much less is known about the mechanism of electronic sputtering of large (bio-)molecules. Most measurements refer to the ionic component, but recently, sputter yields of $\sim 10^3$ leucine molecules have been reported [205] for bombardment with 90 MeV iodine ions. This implies a fairly large interaction region for each bombarding ion, the pertinent surface area having a diameter of at least 100 Å. With such dimen-

sions, early attempts to explain molecule emission in terms of the *primary* interaction of the impinging ion with the target molecules [324–326] appear less feasible than others taking into account secondary processes as a means of energy transport [310,312–317,327].

It has been implied, more or less explicitly [203,301], that the sputtering of large biomolecules is closely related to the sputtering of ices, one indication being similar scaling properties of yield versus energy curves for fission fragment type of bombardment [333]. While there does not seem to be any evidence to the contrary, presently available models for the two types of processes do not have much in common with regard to the respective energy pathways. One issue of interest in that connection is the respective size of the sputtered species. While the sputtered flux from ices is known to contain a sizeable fraction of large clusters for keV bombardment [24], similar evidence from high-energy experiments does not seem to be available.

7. Concluding remarks

One striking development during the past decade is the large *computational* effort in sputter theory (as well as other branches of physical science). Although this feature has been discussed and commented in some detail [33], I wish to contribute a few remarks based on experience acquired in working with the present article.

Firstly, as was mentioned already in the introduction, almost all simulational work has concentrated on knockon sputtering in the linear cascade regime, i.e. a regime where the basic physics is reasonably well-established and where the computational procedure is rather straightforward. Very little has been contributed to modelling less well-known processes like electronic sputtering and nonlinear cascades, the exception being in molecule sputtering where computational and analytical efforts were reasonably well balanced. From a general point of view, model-making is a strength of computational physics. There is no reason why this approach should be less successful in areas where simple Newtonian mechanics is not the penultimate tool.

Secondly, most simulation papers offer package deals, i.e., you get a sputter yield, a spectrum or alike, evaluated for a certain set of assumptions, take it or leave it. If you want to change one parameter, say, the screening radius in the target–target potential, the computation usually needs to be done over again from the beginning despite the fact that ion–target collisions proceed unchanged.

All simulation codes offer rich possibilities of plotting intermediate results. It is up to the physicist to extract pertinent intermediate results such as primary recoil spectra versus depth, ejection probabilities versus depth of origin, and alike, to find proper scaling laws

allowing interpolation and to avoid redundant computing. Splitting up into modules facilitates comparison of different codes with each other, as well as with analytical predictions and experiment. It also enables one to establish a practical database. Examples of surprisingly good agreement between simulation and analytical estimates have been mentioned in sections 2.1, 2.2 and 3.1., and several other examples such as ref. [334] versus refs. [150,335] could readily be added.

It is the declared purpose of many simulation codes to provide theoretical estimates that do not suffer from the shortcomings of various analytical approaches such as high-energy expansion, power cross section, infinite medium and alike. In view of this, it is surprising how comparatively small an effort has been directed to test the validity of specific assumptions in the analytic theory by simulation.

One obvious way of splitting up a sputter simulation is a three-step structure with the ion–target interaction being first, the large-scale structure of the primary-recoil cascade (nuclear or electronic) next, and the ejection event last. The applicability of analytical transport theory, Monte Carlo simulation, binary collision lattice simulation, and molecular dynamics follows roughly the same order. In the (no longer exotic [336,337]) case of sputtering by GeV ion bombardment, the primary cross sections may be so small that transport theory is the only feasible tool to treat the primary interaction, yet primary recoil cascades may have sufficiently high energy to make conventional analytic estimates questionable, thus encouraging a binary collision simulation. Molecular dynamics, on the other end, would be prohibitive for either process but well applicable to simulate the ejection [331].

A major aim of future computations may be systematization of the output in terms of statistical parameters [338] and economic combination of different simulational tools [339].

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