Introduction to Sputtering

Peter Sigmund

Physics Department, Odense University

DK-5230 Odense M, Denmark

Synopsis

The main purpose of this brief tutorial is to give some guidance and reading help to the nonexpert who wants to utilize the present volume as an introduction to the field of sputtering. That field has a long history, yet the present book has been planned to cover primarily developments over the past ten years. Some basic terminology is introduced and a rough classification of the field is given. A few central references to the older literature have been listed and commented on. They are not meant to be comprehensive, but many of them are classics in the field or important sources of background information. The main function of these references should be to provide access to well-established knowledge which, more or less explicitly, enters as a common background into many of the contributions in this volume. In addition, a few hints on key applications of sputtering have been included.

1 The Phenomenon

Sputtering is the erosion of material surfaces by particle impact. The variety of materials for which sputtering has been or can be observed is virtually unlimited. The standard source of bombarding particles in the laboratory is a collimated ion beam with a well-defined energy, but both electrons and photons as well as neutrons and other particles may give rise to sputter phenomena. In applications of sputtering, and wherever the phenomenon occurs in nature, a very wide variety of bombardment conditions must be envisaged.

Sputtering is a phenomenon on the atomic scale. By this is meant that one can identify an individual sputter event, i.e., the emission of a number of atoms or molecules from a material surface initiated by a single bombarding particle. It is the physics of this individual sputter event which is the most fundamental process in sputtering and the main subject of many of the contributions to this volume. A sputter event is a priori statistical in nature. However, after bombardment with a great number of particles, macroscopic effects such as a change in weight

will be observed, and a crater may be visible on the target area facing the beam. Such macroscopic phenomena are quasi-deterministic and allow the operational definition of terms such as erosion rate and sputter yield that will be discussed below.

Not all particle-induced erosion is called sputtering. If an intense beam deposits energy at a rate high enough to heat the entire target surface to near or above the boiling point, the resulting erosion by evaporation is not classified as sputtering. Clearly, this cannot be considered as a superposition of microscopic erosion effects caused by individual bombarding particles. Nonetheless, part of the observed erosion may well be caused by sputtering.

Sputtering is a ubiquitous phenomenon whenever energetic particles interact with materials, and the effect has many applications. Therefore, the term is utilized in different meanings by different communities. Those who use sputtering as a means of etching, cleaning, or polishing materials may use sputtering synonymously with 'bombarding with an ion beam'. The community of researchers and engineers who use sputtering instead of evaporation in the deposition of thin films use sputtering synonymously with 'sputter-depositing'. Historically, the term came up early in this century to illustrate the elementary event which was thought to resemble what happens when a stone falls on a water surface.

2   Quantification

Until little more than a decade ago, weight-change measurements were the main experimental tool in the quantification of sputter processes. For most of a century, such measurements were performed by literally weighing a target on a more or less sensitive scale before and after exposition to a source of energetic ions. Such measurements provide the 'sputter rate', i.e., the change in coverage [atoms per unit area] per unit time. They allow a comparison between sputter properties of different materials. When the bombarding beam is well defined and the current measurable, one may convert sputter rates into 'sputter yields', i.e., the mean number of target atoms (or molecules) sputtered per incident beam particle.

The key quantity characterizing the beam is the fluence, i.e., the number of incident particles per area. The fluence is the integral over time of the particle current density. Measurements of sputter parameters at low fluences are of prime interest in the study of fundamental sputter processes.

The sensitivity of weight-change measurements was greatly improved when targets deposited on a quartz crystal microbalance were inserted into the vacuum chamber. The fact that target preparation, ion bombardment, and measurement of sputter effects all can be performed in situ without breaking the vacuum removed

a major source of experimental error, allowed for measurements at low fluences, and reduced the time needed to collect a given amount of data by several orders of magnitude.

Tabulations of sputter rates and yields for elemental targets were compiled regularly, starting with Crookes (1891). A critical and comprehensive compilation of elemental sputter yields along with an extensive discussion of requirements for reliable measurements may be found in a review by Andersen & Bay (1981).

Several alternative techniques are available for experimental determination of sputter rates and yields. Sputtered material may be deposited on a collector and quantified by weight change of a quartz crystal microbalance, by surface analytical techniques, by means of radioactive tracers, by dissolution and chemical analysis, and the like. Most of these techniques also provide differential information on the angular emission pattern of the sputtered particles as well as the chemical composition of the sputtered material in case of a multicomponent target such as an alloy, a compound, or an isotopic mixture. Pertinent data and techniques have been reviewed by Hofer (1991).

Direct analysis of the flux of sputtered particles is also possible. It is important to note that for a very wide variety of target materials, the vast majority of sputtered atoms or molecules is emitted as neutrals, although not necessarily in the ground state. Moreover, typical energies of sputtered particles lie in the lower eV region. Therefore, efficient use of conventional detection techniques for fast particles requires post-ionization and/or acceleration of sputtered particles. Typical tools for postionization are electron beams, gas discharges, and laser beams.

Laser beams have proven to be a very versatile tool for experimental research in sputtering. Sputtered atoms or molecules may be excited resonantly. For a reasonably narrow absorption line, the Doppler shift corresponding to the translational velocity of an ejected atom lies outside the resonance. Therefore, laser resonance fluorescence provides direct information on the velocity spectrum of emitted particles. By suitable combination of lasers, such information may be gained for several species present in and emitted from a multicomponent target. This information is state-specific. By use of apertures or appropriate optical techniques, also dependencies on emission angle may be studied. By means of multiphoton ionization, the detection sensitivity may be increased by many orders of magnitude. Pertinent information may be found in reviews by Hofer (1991), Gruen et al. (1983), and the contribution by WINOGRAD to the present volume. The review by Hofer (1991) also presents information on non-laser-based techniques for determining energy spectra of sputtered particles. Most of them rely on flight-time measurements.

Observation of eroded surfaces provides valuable information on sputter processes, but until recently, such information was available only on a rather large length scale. It has been known for a very long time (Günterschulze & Tollmien,
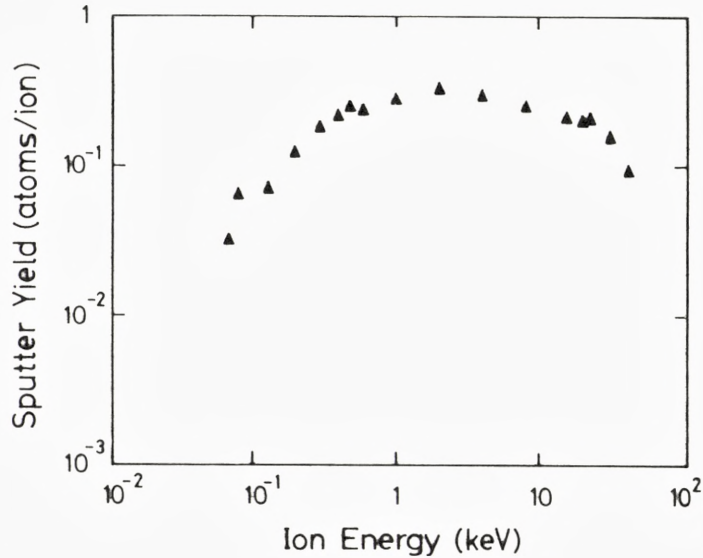
Figure 1. Sputter yield versus beam energy for He$^+$ on Cu. From Roth (1980).

1942) that metal surfaces develop peculiar topographies during prolonged sputtering: A sputtered crater may contain cones, pyramids, and ridges with dimensions ranging from several microns down to a few hundred Ångströms or less (Carter et al., 1983). Formation of surface structures on such a scale is unquestionably a high-fluence phenomenon dependent also on other material properties than those governing the individual sputter event. Observational techniques have now been refined to a stage where inspection of craters formed by individual ion impact down to atomic size is possible. Recent work in this rapidly developing field has been summarized by TSONG & BEDROSSIAN in this volume.

Surface analytical techniques such as Rutherford backscattering, Auger spectroscopy, or ion-surface scattering may be applied to the study of a bombarded target surface. Such measurements provide insight into near-surface changes in chemical composition of a multicomponent target caused by sputtering and other processes initiated by bombarding ions. Pertinent experimental techniques as well as data on 'partial sputter yields', i.e., sputter yields for individual species, have been summarized by Betz & Wehner (1983). A follow-up with the emphasis on the theory of compositional changes is given by LAM and myself in the present volume.

This brief survey is by no means complete: Not all experimental techniques utilized in sputter research have been mentioned, and the catalogue of measurable
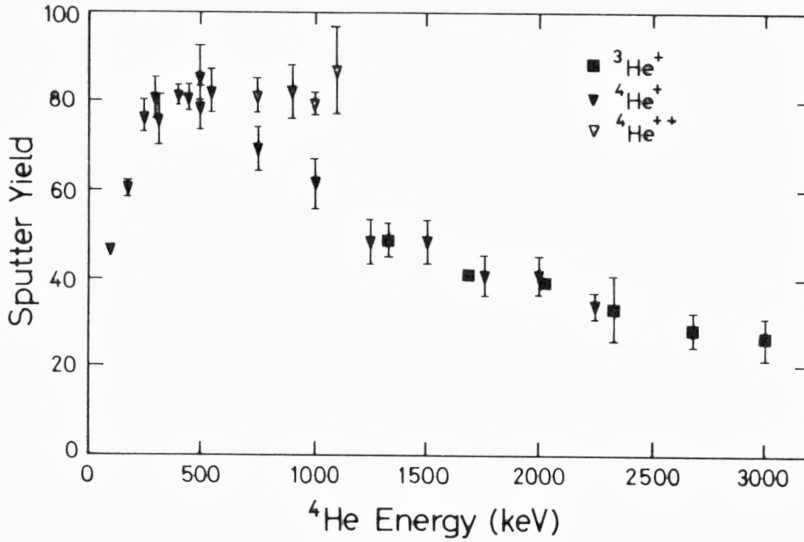
Figure 2. Sputter yield versus beam energy for He$^+$ on solid Ar. From Besenbacher et al. (1981).

parameters is not comprehensive. Nevertheless, an attempt has been made to give an indication of the level of detail at which sputter phenomena have been and can be studied experimentally. For a more comprehensive picture, the reader is referred to the experimentally-oriented contributions to Behrisch (1981, 1983a) and Behrisch & Wittmaack (1991) as well as the present volume.

3   Main Observations

The lowest recorded sputter yields have been measured for neutron bombardment: Values of $\sim 10^{-5}$ sputtered metal atoms per incident fast neutron seem common (Behrisch, 1983b). Very high sputter yields, of the order of 10^3 or more atoms or molecules per ion, have been reported for bombardment of insulating targets with swift ion beams at fission-fragment energies on the one hand, and for bombardment of conducting targets by large clusters with lower energies on the other. Pertinent summaries are found in the contributions of JOHNSON & SCHOU and ANDERSEN, respectively, in this volume.

There is usually a threshold value for the beam energy above which sputtering sets in. Conversely, sputter yields tend to decrease at high energies. The physics of the threshold is governed by energy and momentum conservation laws of the

processes leading to sputtering. The decrease at high energies reflects a general property of the pertinent collision cross section, e.g., Rutherford's law in case of charged-particle bombardment.

Figures 1 and 2 show sputter yields versus projectile energy measured for He^+ bombardment of copper and solid argon, respectively, at normal incidence. While the two curves have qualitatively similar appearances, the difference in both ordinate and abscissa scale is astonishing. It indicates that we deal with entirely different mechanisms of sputtering in the two situations. Inspection of pertinent data on ion penetration shows that the energy dependence of the sputter yield of Cu resembles the behavior of the energy lost to elastic collisions, the 'nuclear stopping power' of a moving ion. Conversely, the sputter yield for the argon target follows the behavior of the electronic energy loss, or 'electronic stopping power'. This difference is crucial to all modern research in sputtering. It was not recognized until the end of the 1970s because until then, well-controlled sputter experiments were performed mainly on metallic targets where sputtering by elastic collisions, 'collisional sputtering', dominates. Up till now, electronic sputtering has been identified unambiguously only on certain insulators. Although that field has been summarized at regular intervals, the paper by JOHNSON & SCHOU in the present volume is probably the most comprehensive survey of both experiment and theory as well as the interface to collisional sputtering.

Sputter yields have of course been measured as functions of the angle of incidence of the beam. For polycrystalline and amorphous materials, the sputter yield tends to increase with increasing oblique incidence up to a certain maximum, and to decrease at glancing incidence. The behavior reflects that of the expected density of energy deposition in the pertinent surface layer where processes occur that lead to sputtering. In case of crystalline materials the behavior is more complicated, and several pronounced minima and maxima in the dependence of the sputter yield on the angle of incidence are usually found. Minima are observed for bombardment along closely-packed directions where ions may be steered into open channels without undergoing collision events that are dramatic enough to cause emission of atoms or molecules from the surface. Most pertinent experimental work on single as well as polycrystals dates back to more than a decade ago and has been reviewed by Roosendaal (1981) and Andersen & Bay (1981), respectively.

Several material and beam properties determine the absolute magnitude of the sputter yield at a given energy and direction of incidence. In general, sputter yields increase with increasing volatility of the bombarded material. This is intimately related to the fact that energy spectra of sputtered atoms are dominated by 'low' energies, i.e., energies very near the threshold energy that allows an atom or molecule to be emitted. The physics of the effective surface binding energy in sputtering is a somewhat delicate subject, to which viable theoretical approaches
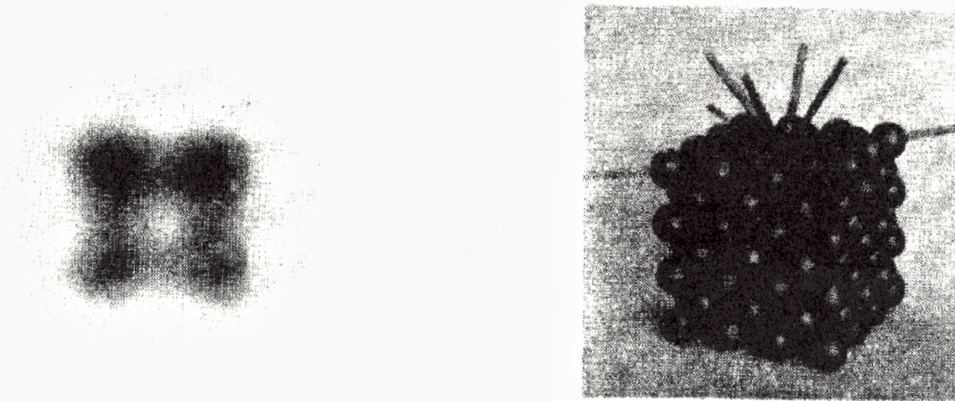
Figure 3. Emission pattern measured on a (100) Ag crystal bombarded by 100 eV Hg ions. From Wehner (1955).

have been developed only very recently, cf. contributions by NIEMINEN, ROBINSON, and SIGMUND & LAM to this volume. There is, however, clear evidence to support the notion that the effective surface binding energy does not differ dramatically from the heat of sublimation. In collisional sputtering, the maximum attainable energy of a sputtered atom may come close to the maximum transferable energy in an elastic collision between a beam particle and a target atom. In electronic sputtering, an upper limit could be set by the energy stored in an individual electronic excitation. In either case, this maximum may exceed the surface binding energy by orders of magnitude. If so, available energy tends to be shared, either collisionally via 'collision cascades' or electronically via 'ionization cascades'. One implication of this cascading process is the possibility of sputter yields $\gg 1$. Another implication is the dominance of low energies in the spectrum of emitted particles, and hence the dominating influence of the surface binding energy on the magnitude of the yield.

Closely related to energy spectra is the subject of angular distributions of sputtered particles. Dramatic effects are observed first of all under bombardment of single crystals. In fact, the observation of 'spot patterns' of ejected material by Wehner (1955), which closely reflect the crystal structure of the bombarded target (fig. 3), may well be considered to signalize the beginning of modern research in sputtering. Distributions in energy and emission angle of particles sputtered from elemental materials have been reviewed by Hofer (1991). Crystal lattice effects specifically are addressed by WINOGRAD in the present volume.

Reliable measurements on the state of aggregation as well as the state of excita-

tion of the flux of sputtered material have become possible, and systematic trends are coming up slowly. Atoms, molecules, clusters, and large aggregates have all been identified in the sputtered flux from a variety of materials under a variety of bombardment conditions. In addition to the (usually) dominating neutral component, both positively and negatively charged species are well known to contribute. In fact, even though the charged component is a minority, it has been analysed in much greater detail for many systems since standard mass spectrometric techniques can be applied. This is particularly true for organic materials, as seen in HÅKANSSON's and ENS' reviews in this volume. The matter becomes more complicated in case of the neutral flux where recording a mass spectrum may require postionization which is a violent process from the point of view of molecular stability. Nevertheless, with increasing sophistication of experimental techniques, a trend is visible toward the recognition that molecules and clusters may constitute a very substantial fraction of all emitted material. This, in turn, sets question marks with experimental techniques that rely on the assumption that the majority of the sputtered material is ejected as atoms. Emission of molecules and clusters from inorganic materials has been summarized by URBASSEK & HOFER in the present volume. For organic materials, emission of molecules and molecular fragments is the prime subject of investigation, and atoms play only a very minor role. Therefore, the contributions by REIMANNN, HÅKANSSON, ENS, and KARAS to this volume all deal with this subject.

Very little is known about the neutral component in the sputtered flux from organic targets. Conversely, detailed studies are available for the ionization mechanism of particles – mostly atoms – sputtered from metals. This research — triggered by the needs of secondary-ion mass spectrometry (SIMS), a surface-sensitive analysis technique relying on sputtered ions — has been omitted because it is the subject of a whole conference series on Inelastic Ion-Surface Collisions. Major reviews on ionization probabilities of sputtered atoms may be found in IISC (1983, 1987).

4 Theoretical Models

Most of the theoretical modelling of electronic sputter processes has been done rather recently and is summarized in several contributions to this volume. REIMANN's contribution presents an illuminating overview, even though it addresses primarily sputter processes involving large molecules. I find it hard to imagine a better introduction to this complex of problems and, therefore, shall make no attempt to compete. The paper by JOHNSON & SCHOU emphasizes processes in condensed gases, in particular noble gases: This is the only class of material where there has been achieved a general consensus about some of the processes responsible
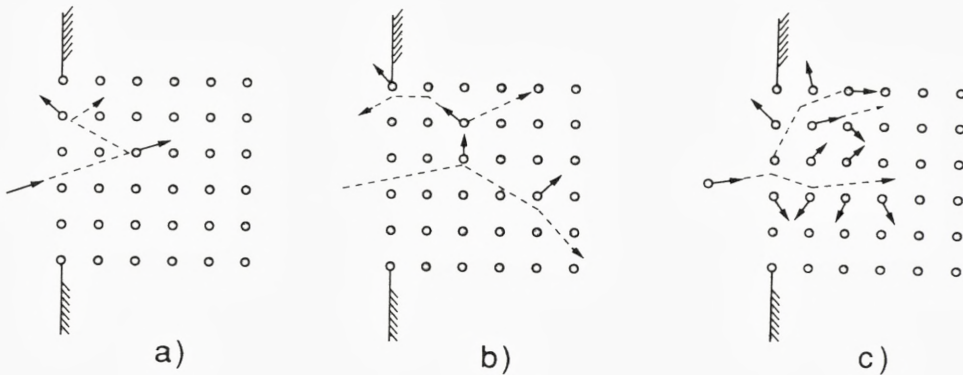
Figure 4. Three representative cases of collisional sputtering. a) Low-yield regime; b) Linear cascade; c) Spike regime. From Sigmund (1981).

for sputtering. SZYMONSKI discusses ionic crystals: Electronic sputtering from these materials has been discussed for several decades. A review of earlier work was given by Townsend (1983). Attempts to model laser-induced sputter processes on more general considerations are discussed by HAGLUND & KELLY.

There appears to be a general consensus that electronic sputter processes are heavily material-dependent not only quantitatively but even qualitatively. Therefore, very little can be said about electronic sputtering in general, and the shape of a yield curve like the one shown in figure 2 cannot be said to be universal.

The situation is very different with regard to collisional sputtering: If an adequate amount of kinetic energy can be transferred to a target atom by an incident projectile, this energy is shared with other atoms in secondary collisions. Some of those may lead to ejection of atoms. The quantitative details of this sequence of events depend more or less sensitively on all bombardment parameters, but the qualitative features are rather independent of the material. The physics of these collision cascades has been investigated for many years, and most of the fundamental concepts were well established decades ago. This knowledge enters more or less implicitly into several contributions in this volume, including those dealing with electronic sputtering processes. A brief introduction may therefore be appropriate.

Fig. 4 shows three prototypes of collisional sputtering. Fig. 4a illustrates a low-yield event which could represent the case of a heavy metal bombarded by a low-energy (< 1 keV) H^+ ion. The maximum energy transferable to a target atom is only a few electron volts, but the projectile has a high probability for wide-angle deflection according to the cross section for elastic scattering on an appropriately screened Coulomb interaction potential. Therefore, a projectile ion may return to

the surface and transfer an adequate amount of energy to a target atom to enable it to overcome surface binding forces. The sputter yield for this type of event will usually be < 1, possibly $\ll 1$.

With increasing ion energy, the cross section for wide-angle scattering decreases but the maximum transferable energy increases. Sputter yields increase initially, as is seen in figure 1. This increase is caused by formation of collision cascades, i.e., the efficient dissipation of primary recoil energy amongst target atoms so that a large number of them have energy enough to be emitted. It is, then, a matter of the configuration in space how large a portion of those recoil atoms is close enough to the target surface to be ejected. Atoms recoiling from lattice sites remote from the surface cannot be ejected but tend to form defects, i.e., vacancies and interstitials and their conglomerates.

Figure 4b illustrates a 'linear collision cascade'. The main feature here is a comparatively long mean free path between energy-dissipating collision events. This has the effect that only a small fraction of the atoms occupying any simply connected volume is set in motion with a noticeable energy. The main characteristic of a linear cascade is an approximately linear dependence of the number of participating target atoms on the available kinetic energy. This is extremely useful for providing pertinent theoretical estimates on sputtering.

Figure 4c illustrates the opposite extreme of a 'collision spike'. Here the mean free path between recoil-generating collisions is so small that essentially every atom in a certain volume is set in motion. The spike volume is determined primarily by the range of the ion which depends on energy in a well-defined manner. Therefore, the number of atoms set in motion cannot be expected to be proportional to the available energy in this case.

The distinction between a linear cascade and a spike is ultimately a matter of definition of the critical energy above which an atom may be said to be in motion: If that energy is chosen high enough, any cascade will be linear. Conversely, that energy can be chosen small enough so that every cascade takes on the properties of a spike. With regard to sputtering, a reasonable choice of the threshold energy would appear to be the surface binding energy U which is typically a few electron volts. This topic has been discussed extensively by the present author (Sigmund, 1977).

Linear cascades and spikes show a different behavior with regard to sputtering. In case of a linear cascade, sputtering is little more than the intersection of a collision cascade with a target surface: The processes leading to transport of an atom toward the surface and subsequent ejection are essentially the same as those that characterize the development of the cascade as a whole. Conversely, transport of matter, energy, and momentum must proceed more collectively in case of a spike. There is, in fact, no unanimous agreement about the hierarchy of processes in a

spike and the respective contribution to the sputter yield. One school of thought advocates heat transport and subsequent evaporation to be the dominating feature. Other schools operate with shock waves (or pressure pulses). Some of those features have been discussed by REIMANN, JOHNSON & SCHOU, and ANDERSEN in this volume.

Experimentally, the linearity of a cascade may be verified by bombardment with polyatomic ions. Incident molecules tend to dissociate upon impact with the target surface, and the fragments tend to follow their individual, stochastic trajectories. These trajectories are, however, confined to roughly the same target volume. In the cases illustrated in figs. 4a and 4b, the number of target atoms set in motion by a diatomic molecule will, to a good approximation, be twice as large as for monoatomic bombardment at the same projectile speed. Conversely, in case of fig. 4c, about the same number of atoms will be set in motion for monoatomic or diatomic bombardment. In the absence of competing transport processes, one expects an unchanged sputter yield per projectile atom for the low-yield case and the linear cascade, and a lower sputter yield per projectile atom in the case illustrated in figure 4c.

Pertinent measurements have been performed long ago and are summarized in ANDERSEN's contribution to this volume. For ions of low mass and atomic number, sputter yields per incident atom tend to remain constant, thus confirming linear-cascade behavior. For ions of high mass and atomic number, as well as large polyatomic ions, sputter yields per incident atom tend to be larger than for monoatomic bombardment. This suggests that additional transport mechanisms beyond energy dissipation in linear cascades must contribute to sputtering in case of high density of energy deposition.

5   Theoretical Tools

A complete, quantal calculation of a sputter event has never been performed on any system. It is not even evident whether anybody at present judges such a calculation to be necessary or desirable.

A convenient way of splitting up the physics of a sputter event is a three-stage process consisting of

  I) slowing-down and energy dissipation of the primary particle,

 II) cascade processes and transport, and

III) particle escape from the surface.

There is no strict separation between the three stages, and the separation may not even be visible in a given calculation, but different input is clearly required. At

any rate, it is desirable to know where to look for inadequate input when there is poor agreement between theory and experiment.

The physics of the first stage (I) belongs to the field of particle penetration phenomena which is highly developed. Pertinent cross sections for elastic collisions and electronic excitation or ionization are available for all projectiles at all energies, although data tend to be less reliable in the lower keV range and below, especially for projectiles of high mass and atomic number. The classics in the field are Bethe's theory of the stopping power of a light ion (Bethe, 1930) and the LSS theory of heavy-ion ranges (Lindhard et al., 1963). Numerous reviews are available. I should like to mention Fano (1963), Inokuti (1971) and Sigmund (1975) on electronic stopping, and Sigmund (1972, 1983) on range theory.

Particle stopping and scattering as well as related processes like sputtering are multiple-collision phenomena. The stochastic nature of these processes suggests the use of bookkeeping techniques which are familiar from numerous branches of physics. Similar techniques are needed in the description of the second stage, but the merits of different approaches depend on the pertinent energy range as well as the required job. Bookkeeping procedures may be roughly classified into four categories,

- Linear transport theory,
- Monte Carlo simulation,
- Binary collision simulation,
- Molecular dynamics simulation.

Linear transport theory and Monte Carlo simulation are equivalent in principle. In either case, collision statistics is governed by Poisson's law, with binary-collision cross sections and continuous (frictional) forces being the primary input. The relative merits of the two techniques are easily identified: There are virtually no limits on the variety of quantities that can be evaluated by Monte Carlo simulation for a given geometry. Conversely, atomistic input is predominantly available in the form needed for transport calculations, i.e., stopping power, energy loss straggling, etc., while fully differential cross sections — which enter into genuine Monte Carlo simulations — are more sporadically tabulated. Most of the computation time in standard Monte Carlo simulation codes is wasted on insignificant collision events. Despite this, their statistical accuracy is usually higher than that of the other two simulation methods.

Binary-collision simulations differ from Monte Carlo simulations by the introduction of a prescribed target configuration. Such simulations are useful whenever crystal lattice effects are judged to be important. For the slowing-down stage, this is vital in attempts to predict the dependence of the sputter yield on angle of

incidence.

Molecular-dynamics simulations operate on the basis of Newton's equations which are solved simultaneously for the projectile-target many-body system. Computational capacity restricts the applicability of this technique to fairly low primary-beam energies with regard to the treatment of the slowing-down stage (I). For medium-mass ions such as argon, such simulations have rarely been performed at energies exceeding 5-10 keV. For lighter ions at similar energies, penetration depths and pathlengths become exceedingly high and impose even narrower limits on accessible energy.

The three simulation techniques have been reviewed extensively in the contributions by ROBINSON and NIEMINEN to this volume. A contribution about transport theory has not been solicited since most of the fundamental concepts have been developed long ago. They are still valid and have been summarized repeatedly (Sigmund, 1972, 1981, 1987). More recent work is mentioned in proper context in several contributions to this volume.

In stage II, cascade processes and transport, it is necessary to distinguish between electronic and collisional sputtering. In electronic sputtering, energy may be dissipated first electronically and, after having been transferred into nuclear motion, also collisionally. Therefore, both ionization cascades and collision cascades may be important, as may be transport of electronic excitation as well as kinetic energy of atoms and matter. The pertinent collection of theoretical tools depends heavily on the material. As far as transport of atoms is concerned, molecular-dynamics has proved to be a useful tool in addition to classical hydrodynamics. Binary-collision-type of models, regardless of which kind, tend to be less useful in view of the extremely low energies (less than 1 eV per atom) that are frequently involved. As far as ionization cascades and excitation transport are concerned, pertinent theory is available from fields like luminescence physics and radiation dosimetry. References may be found in the contribution by JOHNSON and SCHOU.

In collisional sputtering, the description of stage II is conceptually very simple. The accuracy of the output is limited mainly by the degree of reliability of the pertinent cross sections for elastic collisions or the equivalent interatomic potentials utilized in the calculations. In a collision cascade, particles are followed down to very low energies, and since the number of participating atoms increases with decreasing energy, cross sections at the lowest energies enter with the highest statistical weight. Most important are cross sections in the range from the surface binding energy up to a few tens eV, and these are just about the least well-known ones.

The strength of analytical sputter theory (Sigmund, 1969, 1981) lies in the recognition of two pertinent energy ranges, one of the order of the primary energy and another one of the order of the surface binding energy. The major uncertainty

about the interaction potential can, therefore, be condensed into one single parameter, which happens to be closely related to the depth of origin of sputtered atoms. Some of these points are reviewed in my contribution with LAM to the present volume.

In simulations of sputter events, atoms may achieve any amount of energy from a certain maximum downward. Hence, definite assumptions must enter about interaction forces at any achievable energy. Some progress has been made in the theory of interatomic potentials in particular in metals, including many-body interaction potentials, and this progress is extensively discussed in the contributions by NIEMINEN and ROBINSON. The main strength of many-body potentials is their capability to quantitatively characterize bulk and surface binding forces.

There are some conceptual differences in the characterization of collision cascades between the four available techniques which have been discussed by Andersen (1987) in a very illuminating overview. Comparisons between different simulation codes have been reviewed in ROBINSON's contribution.

As in the case of stage I, the range of applicability of transport theory and Monte Carlo simulation is restricted to materials where lattice structure is not of primary importance. Inspection of fig. 3 indicates that the crystal lattice structure might play a significant role in the development of a collision cascade. In fact, experimental results of the type shown in fig. 3 had a major influence on the direction of research in sputtering for more than a decade starting in 1955. Random collision events were considered only to govern primary interactions, and the dominating means of energy and mass transport was thought to be linear collision sequences, with or without replacement, on close-packed lattice rows. The first molecular-dynamics simulations in the pertinent energy range appeared to confirm the qualitative picture (Gibson et al., 1960). It has since then become clear — as is documented in ROBINSON's contribution — that those simulations overestimated the statistical significance of linear collision sequences. There are two main reasons for this. Firstly, the range of starting directions sampled in a limited number of simulation runs was confined to a single close-packed lattice plane. Secondly, starting energies were not sampled from a representative recoil spectrum. This kind of lesson has probably been learned repeatedly in the history of computational physics.

It was mentioned above that the absolute magnitude of the sputter yield depends on the surface binding energy. A rough, inverse relationship between measured sputter yields and the heat of sublimation has been known for a very long time (Behrisch, 1964), but accurate knowledge of surface binding forces for sputtering was lacking. The standard model was a planar surface potential (Thompson, 1968), similar to the one used in electron emission. More detailed models were based on bondbreaking arguments. Accurate theoretical predictions of forces be-

tween atoms and solid surfaces are now becoming available (Daw & Baskes, 1984; Finnis & Sinclair, 1984, Jacobsen et al., 1987) and may be utilized either directly in dynamic simulations, or indirectly as input into transport calculations or non-dynamic (Monte Carlo or binary-collision) simulations.

6   Theoretical Results

Many well-established results from sputter theory will be quoted more or less explicitly by the authors of the present volume. There are, however, a few central relationships which it may be useful to be aware of from the beginning.

The first is the so-called (energy)$^{-2}$ law which dates back to Robinson (1965). This fundamental property of linear collision cascades shows up on numerous occasions, expected or unexpected, rigorous in some connections, approximate in others. For detailed discussion, the reader is referred to Sigmund (1972, 1981). The most rigorous result refers to the 'recoil density', which may be defined as the mean number of atoms recoiling with an energy in the interval $(\epsilon, d\epsilon)$ as the result of the slowing-down of a primary ion of energy E in an infinite, monoatomic, random medium. That quantity is given by

$$F(E, \epsilon)d\epsilon \sim \Gamma\frac{\nu(E)}{\epsilon^2}d\epsilon \text{ for } E \gg \epsilon, \tag{1}$$

where $\nu(E)$ is the portion of the initial energy E which is not transferred into electronic excitation, and Γ is a constant depending somewhat on the atomic interaction potential. The important feature is that the detailed nature of the elastic-scattering cross section only enters into the factor Γ but not into the dependence on recoil energy ϵ. While the above result has been derived on the basis of linear cascade theory, i.e., for long quasi-free flight paths and point particles, the simple analytical form suggests it to be more general. In fact, recoil spectra extracted from computer simulations confirm this behavior, even for crystalline targets and at quite low primary energies.

While the recoil density is a central quantity in sputter theory, it is only indirectly related to measurable energy spectra of sputtered atoms. Nevertheless, the latter spectrum is also frequently denoted as an (energy)$^{-2}$ distribution. The spectra differ because of the effect of (bulk and) surface binding forces as well as the fact that the flux of sputtered atoms has contributions from several atomic layers beneath the surface, the relative significance of which depends on energy but decreases rapidly with increasing depth of origin. The recognition of both features dates back to Thompson (1968).

Consider first the effect of a planar surface potential U. If the energy spectrum of atoms arriving at the target surface were given by ϵ^{-2}, an atom moving at an

angle θ to the surface normal would be emitted at an angle θ' and energy ϵ' given by the relations

$$\epsilon' = \epsilon - U; \ \epsilon' \cos^2 \theta' = \epsilon \cos^2 \theta - U, \tag{2}$$

and the energy spectrum of sputtered atoms would read

$$Y(\epsilon') \propto \frac{\epsilon'}{(\epsilon' + U)^3} \tag{3}$$

for an isotropic flux of atoms within the target. This 'Thompson spectrum' is the common reference standard for measured energy spectra of sputtered atoms (Gruen et al., 1983). It has frequently served as a tool for 'experimental' determination of surface binding energies. The main objection to this scheme is that the Thompson formula implies a cosine distribution of the sputtered flux which is rarely observed experimentally.

The contribution from deeper layers to the sputtered flux can be evaluated easily (Thompson, 1968; Sigmund, 1981). If surface binding is ignored, this results in the expression

$$Y(\epsilon) d\epsilon \propto \frac{1}{\epsilon S(\epsilon)} \tag{4}$$

for the spectrum of sputtered particles, i.e., one factor ϵ has been replaced by the stopping cross section $S(\epsilon)$ of a moving target particle. At low energies, $S(\epsilon)$ is not too far from $\propto \epsilon$, hence the difference is hard to identify. At high energies, $S(\epsilon)$ decreases with increasing energy, and the denominator in eq. (4) will vary very slowly. As a result, one expects the spectrum to level off. This behavior, expected to be observable in sputter experiments at high-energy heavy-ion accelerators such as GSI or GANIL, is worth remembering. Such extreme experimental conditions are not foreseen in conventional computer simulation codes.

7   Sputtering in Nature, Science, and Technology

A monograph with such a title has never been written to the author's knowledge but could be very stimulating reading. As in other parts of this introduction, I shall try to provide a few keywords and key references rather than go into a detailed listing or even discussion of occurrences and applications of sputter phenomena.

There is no doubt that sputter phenomena have played and still play a major role in stellar and planetary processes. Observational studies refer to planetary bodies such as meteorites, the Moon, and Jupiter's satellites. Sputter erosion of the Moon by solar-wind bombardment was first mentioned by Wehner et al. (1963). Interest in this type of phenomenon was greatly intensified by the discovery of electronic sputtering from water ice (Brown et al., 1978) as well as the observation

of isotopic anomalies in meteorites and lunar samples. Pertinent reviews have been provided by Johnson (1990) on the former complex of problems and by TOMBRELLO in this volume on the latter.

While appearances of sputter phenomena on planetary bodies exposed to external irradiation are commonly thought to be restricted to those that do not carry an atmosphere, it was demonstrated that planetary atmospheres also may erode by sputtering due to the action of the solar wind and solar flares (Haff et al., 1978). Several features of conventional collision cascade theory apply to this system, and 'surface' binding energies equivalent to escape velocities from the gravitational field may even be comparable in magnitude with those encountered in conventional sputtering.

Sputter phenomena are an inevitable by-product of radioactivity. Heavy recoil atoms from α decays may cause violent sputter events which are responsible for the high volatility of radioactive materials (Riehl, 1963). Emitted α or β rays may give rise to pronounced electronic sputtering along with other radiation effects, dependent on the pertinent material. Such processes have been intensely studied in connection with the isolation of radioactive waste (Chakoumakos et al., 1987; Matzke, 1992).

As mentioned above, sputter yields for bombardment with (fast or thermal) neutrons are very small, but sputter rates may be substantial in the presence of high neutron fluxes such as in fission and fusion reactors (Behrisch, 1983b). Specifically for fusion reactors, the problem of plasma-wall interaction has a substantial component of sputter-related processes which has been the subject of major national and international research programs (Engelmann, 1986). Typical candidates for first-wall materials are metals, alloys, and carbon-based materials. Mostly collisional sputtering is of concern here because it is unavoidable, while chemical erosion effects are expected to be controlled. Electronic sputtering, on the other hand, is a key process connected with the injection of fuel into the fusion plasma in the form of pellets of solid hydrogen (Chang, 1991).

Probably the earliest technological application of sputtering is the deposition of thin films by collection of the sputtered flux from one or several bombarded materials. Wright (1877) produced films of hitherto unseen smoothness of a large number of metallic elements and pointed at important applications such as coating of astronomic mirrors and the like. This area has developed to major technological importance, reaching from coatings on large glass windows, photographic lenses, and razor blades to contacts on integrated circuits. More recently, production of alloys and compounds such as conventional low-temperature and ceramic high-temperature superconductors has come into focus (Geerk et al., 1989).

Sputtering has long been useful as a tool of etching, polishing, and cleaning material surfaces. This topic has been discussed by TAGLAUER in this volume.

A sputter gun is a standard piece of equipment on ultrahigh vacuum systems. It is utilized universally as a tool of initial sample preparation, in particular surface cleaning, and secondly for analytic purposes.

Sputtering as an analytic tool has revolutionized several scientific disciplines. In sputter profiling, sputtering is utilized as an etching technique in conjunction with any technique to determine the bulk or surface composition of a material. Originally, the technique was developed to determine depth profiles of implanted radioactive tracers (Lutz & Sizmann, 1964). Presently, Auger lines form the standard signal in the technique, as described by TAGLAUER in this volume.

Analysis of the composition of the sputtered flux from a material provides information on its composition. In case of an inhomogeneous material, analysis of the sputtered flux as a function of irradiation time or fluence provides information on the depth profile. Standard techniques go under the headings of secondary-ion mass spectrometry (SIMS), secondary neutral mass spectrometry (SNMS), accelerator mass spectrometry (AMS), plasma desorption mass spectrometry (PDMS), and fast atom bombardment (FAB). TAGLAUER's contribution focuses on several analytic aspects related to inorganic materials. Applications related to biological materials are connected to the contributions by ENS, HÅKANSSON, and KARAS to this volume. All these techniques are extremely useful but have severe problems with regard to quantification. Indeed, there are problems both in the relation between the composition of the sputtered flux and the composition of the bombarded material, and in the relation between the composition of the sputtered flux and the measured signal. The wide application of these techniques provides a major stimulus to theoretical and experimental research on fundamental processes in sputtering.

Acknowledgements

References

Andersen HH, 1987: Nucl. Instrum. Methods B **18** 321
Andersen HH and Bay HL, 1981: in Behrisch (1981), p. 145
Behrisch R, 1964: Ergebn. Exakt. Naturwiss. **35**, 295
Behrisch R, 1981: *Sputtering by Particle Bombardment I*, Top. Appl. Phys. **47** (Springer, Heidelberg)

Behrisch R, 1983a: *Sputtering by Particle Bombardment II*, Top. Appl. Phys. **52** (Springer, Heidelberg)

Behrisch R, 1983b: in Behrisch (1983a) p. 179

Behrisch R and Wittmaack K, 1991: *Sputtering by Particle Bombardment III*, Top. Appl. Phys. **64** (Springer, Heidelberg)

Besenbacher F, Bøttiger J, Graversen O, Hansen JL and Sørensen H, 1981: Nucl. Instrum. Methods **191**, 221

Bethe H, 1930: Ann. d. Physik **5**, 325

Betz G and Wehner GK, 1983: in Behrisch (1983a) p. 11

Brown WL, Lanzerotti LJ, Poate JM and Augustyniak WM, 1978: Phys. Rev. Lett. **40**, 1027

Carter G, Navinček B and Whitton JL, 1983: in Behrisch (1983a) p. 231

Chakoumakos BB, Murakami T, Lumpkin GR and Ewing RC, 1987: Science **236**, 1556

Chang CT, 1991: Phys. Repts. **206**, 143

Crookes W, 1891: Proc. Roy. Soc. London **50**, 88

Daw MS and Baskes MI, 1984: Phys. Rev. B **29**, 6443

Engelmann F, 1986: in *Physics of Plasma-Wall Interactions in Controlled Fusion*, D. E. Post & R. Behrisch, editors (Plenum, New York) p. 15

Fano U, 1963: Ann. Rev. Nucl. Sci. **13**, 1

Finnis MW and Sinclair JE, 1984: Phil. Mag. A **50**, 45

Geerk J, Linker G and Meyer O, 1989: Mater. Sci. Repts. **4**, 193

Gibson JB, Goland AN, Milgram M and Vineyard GH, 1960: Phys. Rev. **120**, 1229

Gruen DM, Pellin MJ, Young CE, Mendelsohn MH and DeWald AB, 1983: in IISC (1983) p. 42

Günterschulze A and Tollmien W, 1942: Zeits. f. Physik **119**, 685

Haff PK, Switkowski ZE and Tombrello TA, 1978: Nature **272**, 803

Hofer WO, 1991: in Behrisch & Wittmaack (1991) p. 15

IISC, 1977: *Inelastic Ion-Surface Collisions*, N. H. Tolk, editor (Academic Press, New York)

IISC, 1981: *Inelastic Particle-Surface Collisions*, W. Heiland and E. Taglauer, editors, Springer Ser. Chem. Phys. **17**

IISC, 1983: *Inelastic Ion-Surface Collisions*, P. Sigmund, editor, Phys. Scr. **T6**

IISC, 1987: *Inelastic Ion-Surface Collisions*, D. M. Gruen, editor, Nucl. Instrum. Methods B **27** no. 1

Inokuti M, 1971: Rev. Mod. Phys. **43**, 297

Jacobsen KW, Nørskov JK and Puska MJ, 1987: Phys. Rev. B **35**, 7423

Johnson RE, 1990: *Energetic Charged Particle Interactions with Atmospheres and Surfaces*, (Springer, Berlin)

Lindhard J, Scharff M and Schiøtt HE, Mat. Fys. Medd. Dan. Vid. Selsk. **33**, no. 14

Lutz H and Sizmann R, 1964: Zeits. f. Naturforsch. **19a**, 1079

Matzke HJ, 1992: Nucl. Instrum. Methods B **65**, 30

Riehl N, 1963: Dechema-Monographien **45**, 77

Robinson MT, 1965: Phil. Mag. **12**, 145

Roosendaal H, 1981: in Behrisch (1981) p. 219

J.Roth, 1980: in Varga et al. (1980) p. 773

Sigmund P, 1969: Phys. Rev. **184**, 383; **187**, 768

Sigmund P, 1972: Rev. Roum. Phys. **17**, 823, 969, 1079

Sigmund P, 1975: in *Radiation Damage Processes in Materials*, edited by C. H. S. Dupuis, NATO ASI Series, Ser. E no. 8 (Noordhoff, Leiden) p. 3

Sigmund P, 1977: in IISC (1977) p. 121

Sigmund P, 1981: in Behrisch (1981) p. 9

Sigmund P, 1983: Phys. Scr. **28**, 257

Sigmund P, 1987: in IISC (1987) p. 1

Thompson MW, 1968: Phil. Mag. **18**, 377

Townsend PD, in Behrisch (1983a) p. 147

Varga P, Betz G and Viehböck FP, 1980: *Symposium on Sputtering* (Inst. f. Allg. Physik, Vienna)

Wehner GK, 1956: Phys. Rev. **102**, 690

Wehner GK, Kennight C and Rosenberg DL, 1963: Planet. Space Sci. **11**, 885

Wright AW, 1877: Amer. J. Sci. **13**, 49; **14**, 169