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**PHYSICAL SPUTTERING
OF ELEMENTAL METALS
AND SEMICONDUCTORS**

by
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1. INTRODUCTORY AND HISTORICAL REMARKS

This overview is not intended as yet another contribution to existing reviews on the physics of sputtering and its history. In this respect, the interested reader is referred to the excellent recent monographs and conference proceedings given in Ref.1 to 5. The intention of this article is to give an introduction to physical sputtering, guided by the interplay between collisional and "thermal" sputtering which has obscured the understanding of the phenomenon since its discovery. It will become apparent that angular distributions of sputtered particles have always played a decisive role in identifying the relevant mechanisms, energy distributions have allowed quantifying them, and mass distributions now urge further efforts towards understanding collective processes.

Sputtering of solids is the emission of surface atoms upon impact of energetic radiation. If we restrict ourselves to metals and semiconductors, "radiation" means particle radiation, first and foremost ion radiation. The phenomenon was discovered in studies of electrical gas discharges about 130 years ago. It took half a century before the nature of the particles involved - ions and electrons in the plasma, to name the modern terms - became clear /6,7/, but from this time on the understanding of sputtering (of cathodes) developed much faster. During the first decade of this century STARK suggested two seemingly opposing mechanisms of surface-atom ejection; it has required intensive research up until recently before a clear answer in favour of one or the other could be given. STARK perceived cathodic erosion by ion impact as either an evaporation/sublimation process from a hot micro-spot /6/, or as a result of a succession of binary collisions during which part of the initial (inwardly-directed) momentum is directed back towards surface atoms /8/.

A thermal mechanism for sputtering was first proposed by HITTORF /9/ who understood cathodic erosion as plain sublimation from cathodes heated in the gas discharge - thus overriding the statement of his former teacher PLÜCKER that particle emission from cathodes is not coupled to the discharge power /10/. GRANQUIST /11/ eventually disproved sputtering as a bulk sublimation process by showing that the yield from externally heated cathodes is largely independent of temperature. - KOHLSCHÖTTER /12/ reviewed the early development up to 1912 and concluded by renouncing his own model in favour of STARK's.

The concept of a hot spot developing around the projectile's point of impact was pursued in various areas of radiation/condensed-matter interaction: by DESSAUER in radiation biology ("Punktwärmetheorie", /13/), by KAPITZA in ion-induced electron emission /14/ and by v. HIPPEL in sputtering /15/.

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2. INFORMATION FROM ANGULAR DISTRIBUTIONS

In 1935 SEELIGER and SOMMERMEIER /16/ performed the first angular distribution studies on polycrystalline and liquid metals. Their results resembled KNUDSEN's cosine-distribution from evaporating liquids so closely that this finding was considered as corroboration of the evaporation-from-a-hot-spot model /17-19/.

It was 20 years before WEHNER's discovery of anisotropic emission from single crystals changed the situation again. In 1955 WEHNER had found that enhanced emission occurs along close-packed lattice directions such as $\langle 110 \rangle$ in fcc and $\langle 111 \rangle$ in bcc lattices /20/. During the following 5 years this effect was confirmed by several researchers over a broad range of impact and target parameters /21-25/. Preferred ejection along close-packed lattice rows is established now over five orders of magnitude of projectile energy, for metals as well as semiconductors and for heavy-ion as well as electron bombardment; it is thus a general irradiation effect in crystalline solids and, since sublimation from single crystals was found to be of a structureless cosine-shape /26,27/, it precludes thermal sputtering's being of a dominant nature.

Fig. 1: Anisotropic emission from single crystals. Emission distribution in the $(\bar{1}\bar{1}0)$ azimuth from $(111)\text{Ag}$ under irradiation with 20 keV Ar^+ ions. The main ejection coincides with the $\langle 110 \rangle$ lattice direction while the weaker maximum is shifted inwards from the $\langle 100 \rangle$ direction, probably due to unbalanced surface collision /29/. From LINDERS et al. /28/.

The discovery of anisotropic emission from single crystals introduced another sputtering concept, that of emission by focusing collision sequences. The controversies over this mechanism have led to the situation that for 20 years single crystal investigations concentrated on particular ejection kinematics (direct or assisted focusing, surface ejection, primary knock-on etc.) /20-38/. Information on the broad areas of physical sputtering, which are: light-ion sputtering, linear cascade sputtering and sputtering from collision spikes, was primarily deduced from polycrystalline targets.

2.1 Emission from Single Crystals

In 1957 SILSBEE /39/ pointed out the possibility of a lattice influence on the energy dissipation of the recoils. In particular, he demonstrated by applying the hard sphere approximation how momentum focusing along $\langle 110 \rangle$ in fcc lattices could be accomplished, provided the interaction potential is sufficiently strong. WEHNER's findings of 1955/56 were not considered as evidence enough for the existence of focusing collision sequences, mainly because of the low (10^2 eV) projectile energies in these experiments. With the confirmation of preferential ejection at higher (10^4 eV) energies /21-25/, however, this restraint no longer applied and focusons became the general interpretation for ejection along close-packed directions. In the hard core approximation it is easy to derive an upper energy limit for collimated recoil momentum transport. This energy is called the focusing energy and is given by

$$E_f = 2A \exp \left(- \frac{D}{2a} \right) \quad (2.1)$$

where A ($A \sim Z^n$, $n > 0$) and a are the parameters of the Born-Mayer potential, and D is the equilibrium interatomic spacing in the row, see Fig.2. Focusing energy values calculated from Eq.2.1 lie about a factor 2 too high compared with more accurate calculations /40,41/, but E_f 's deduced from energy distribution measurements are even larger than the hard-core-approximation values. Hence we consider the following focusing energies for the $\langle 110 \rangle$ direction as acceptable compromises Al:5eV, Cu:25eV, Au:50eV.

Fig. 2: Focusing collision sequence along a close-packed lattice direction. In the hard core approximation momentum alignment is possible only when the collision radius ($2R$) is larger than the half equilibrium distance, i.e. the collision occurs before the saddle-point of the potential of the surrounding lattice.

Rather than arguing about more accurate E_f values, in discussions on the role of focusing collision sequences, it is more constructive to consider also the focuson energy loss, ΔE , to the neighbouring lattice. Both E_f and ΔE increase with the interaction potential (e.g. A in Eq.2.1) and both are, of course, fully subject to its large uncertainties in the 1 to 100 eV energy regime. Since, however, E_f (together with the surface binding energy E_b) determines the fraction of the recoil spectrum contributing to focusing collision sequences, and ΔE determines their length, E_f and ΔE affect the contribution of focusons in opposite ways. The far-reaching potential of Au-atoms, for instance, results in a larger E_f than for Al, but this causes a high ΔE for Au as well. $E_f/\Delta E$, the decisive quantity as regards the con-

tribution of focusing collision sequences to sputtering, is therefore not too different for the aforementioned metals and in no way precludes focuson contributions in Al /42,30/.

For some time, focusing collision sequences were not only regarded as the origin of anisotropic emission from single crystals but also as the main ejection mechanism in general. This transport of energy along correlated collision sequences conflicted with the notion of random collision cascades as being the prime transport mechanism. Thus, for the decision on the starting basis for theoretical treatments, two events in the mid sixties were important:

- SMITH and co-workers /31,32/ stated that even for a pronounced "spot pattern" (this is the deposit distribution anisotropic emission generates on collector plates in the vicinity of the sputtered target) the majority of ejected material is contained in the random, cosine-like background;
- LEHMANN & SIGMUND /43/, and HARRISON et al. /44/ pointed out that anisotropic emission need not necessarily be a focuson effect. The former authors suggested that it might be a consequence of a selective influence of the surface binding energy on the low-energy part of the recoil spectrum, Fig.3. HARRISON et al. found in computer simulations anisotropic emission in the absence of the intersection of the surface by focusing collision sequences.

Fig. 3: Preferred ejection in low-index lattice directions according to LEHMANN & SIGMUND /43/. In the left-hand case surface binding imposes a selection criterion on the impact angles, on the right-hand potential minima between symmetric surface atom arrangements constitute "windows" for low-energy particles. Compared to these selection mechanisms, it is of secondary importance in this model whether or not the collision with the surface atom is focusing ($\theta_2 < \theta_1$). Both mechanisms work only for that part of the recoil energy spectrum which lies near the surface binding energy.

This so-called surface model for anisotropic emission is consistent with the conception of sputtering as being determined by kinetic energy imparted to surface atoms by collision cascades /45,46/. While most of the subsequent angular distribution investigations on single crystals were devoted to determining the respective contributions of the mechanisms causing anisotropic emission as well as their fraction in total emission, sputtering theory based on collision cascades meanwhile found its main support in its good agreement with experimental data of the total yield dependence on the energy, mass and incident angle of the projectile. In SIGMUND's theory of the sputtering of amorphous matter, energy dissipation within the cascade volume is treated by linear Boltzmann equations. Such a linearized trans-

port-theoretical description requires dilute cascades, i.e. cascades where energy can be distributed to an ever increasing number of atoms which were at rest before the collision. Any such dilute or "linear" cascade will eventually transform into a state in which practically all atoms in the slowing-down volume are in motion. Such an ensemble of energetic atoms behaves rather like a high-pressure gas. It is often referred to as a (collision or "thermal") spike.

Fig. 4: Hcp lattices are ideally suited for checking the LEHMANN-SIGMUND ejection mechanism; they show both close-packed lattice rows, $\langle 11\bar{2}0 \rangle$, and pair arrangements without a third partner below the surface, $\langle 20\bar{2}3 \rangle$. Furthermore, the $\langle 0001 \rangle$ lattice direction is a typical case for assisted focusing collision sequences, where an atom is steered by a ring of three neighbouring atoms onto the next atom in the line.

For an investigation of the LEHMANN-SIGMUND model for anisotropic emission, hexagonal close-packed (hcp) monocrystals are the ideal targets: they have both lattice directions allowing momentum focusing, and pairs of atoms where only the surface ejection (LS) model would give an anisotropic component, Fig.4. The existence of preferred ejection from the Zn (0001) plane has been known since the early stages of spot pattern generation /25/; it was in fact mentioned by LEHMANN and SIGMUND as an argument against focusses. But a clear assignment of the respective contributions and degrees of anisotropy required a direct comparison between the $\langle 11\bar{2}0 \rangle$ and the $\langle 20\bar{2}3 \rangle$ emission distribution. This was carried out by HOFER /30/. Figure 5, which is taken from this work, clearly shows the capacity of the surface ejection model. Since, furthermore, the Mg $\langle 11\bar{2}0 \rangle$ emission is identical with the Al $\langle 110 \rangle$ emission it can be concluded that for low-Z elements

- the prime anisotropy-generating mechanism along close-packed lattice directions is the L-S mechanism;
- the contribution of focusing collision sequences to total emission is negligible.

The reason why these investigations were carried out on low-Z crystals is also noteworthy: all medium-to-high-Z hcp metals showed strong ejection along $\langle 0001 \rangle$ /29,30/. This preferred emission, which is of the kind shown in Fig.3b, is highly disturbing for $\langle 20\bar{2}3 \rangle$ investigations. For this reason Mg was chosen, where $\langle 0001 \rangle$ emission is absent; the reason for this in turn is the openness of the lattice - or the weak interaction potential of its atoms; the "surface filter" is too weak. Hence low E_f , low ΔE , and the absence of $\langle 0001 \rangle$ emission from Mg all have the same reason: "the small core size compared to the cell size" /39/ for low-Z crystals. Again we caution, however, not to discard lightly focusing collisions in these lattices! $E_f > E_b$ must hold here, too, otherwise none of the models would explain the

rather sharp spot width; and, as mentioned above, $E_f/\Delta E$ is as large in Al as in Au or Cu.

Fig. 5: Comparison of preferred emission from low-Z single crystals.

a) $\langle 11\bar{2}0 \rangle$ and $\langle 20\bar{2}3 \rangle$ emission distributions from hcp Mg.

For $\langle 20\bar{2}3 \rangle$ only the LS-mechanism, Fig. 3, can cause preferred emission while for $\langle 11\bar{2}0 \rangle$ also focusons can contribute. Their contribution to anisotropy is obviously small, but not negligible.

b) $\langle 11\bar{2}0 \rangle$ emission from hcp Mg and $\langle 110 \rangle$ emission from fcc Al. Both lattice rows are closest-packed and allow focusing collision sequences. From HOFER /30/.

The existence of $\langle 0001 \rangle$ ejection for medium and high-Z hcp crystals together with the total absence of preferred $\langle 111 \rangle$ emission from fcc crystals allows another important conclusion. Since in the two-layer model (LS mechanism) of Fig. 3 these two directions are identical and the difference comes only with the third layer (layer sequence in hcp: ABAB, in fcc: ABCABC ...), the mere existence of potential minima in the top surface layer is not sufficient to explain why there is no preferred $\langle 111 \rangle$ emission; rather the atom to be ejected has to receive its momentum in a directed way such as by virtue of the focusing capacity of the surrounding lattice. Such an assisted focusing emission was first described by NELSON and THOMPSON /23/. It is particularly pronounced for $\langle 100 \rangle$ in fcc and $\langle 0001 \rangle$ in hcp lattices.

At the high-Z end of the stable nuclides, Au has been investigated in great detail /23,33-38/. While the early work was naturally interpreted in terms of the focuson model, SCHULZ and SIZMANN /35,36/ found no feature in extensive studies of the temperature influence on $\langle 110 \rangle$ ejection which was at variance with the surface ejection model. SZYMCAK /37,38/ recently investigated emission from the $\langle 111 \rangle$ surface by varying the projectile energy

over a broad regime (0.1 to 270 keV). Similarly to Ref.32, he tried to unravel the anisotropic component from the random part by fitting analytic functions to the measured distribution. Such a procedure is not unproblematical because a reliable random-fit requires knowing the emission distribution over the full upper half-space /32,28/, otherwise the fit has to be made at an angular region which is most strongly influenced by surface structures; furthermore, a true distinction between random and surface-deflected focusons requires energy-dispersive measurements, see Chap.3. But it is certainly acceptable to deduce from Fig. 6 that even for high-Z elements the majority of particles is ejected randomly. The anisotropic component, however, is no longer negligible. Since the authors conclude that the $\langle 110 \rangle$ ejection is mostly due to focusons, the latter conclusion holds also for these.

Fig. 6: Partial sputtering yields from an Au(111) surface bombarded with Ne and Xe ions. ΔY : random emission, ΔY_{110} : preferred $\langle 110 \rangle$ emissions, ΔY_{100} : preferred $\langle 100 \rangle$ emissions. There is hardly any influence of temperature on partial yields between 15 and 300 K. From SZYMCAK /38/.

The temperature of the target has very little influence on the sputtering of metals. This is true for total and partial yields, as well as for the angular distribution of the random part of the emission, see ROOSENDAL's and HOFER's reviews in Ref.3, and Ref.30-38,47,48. The width of preferred ejection in closest packed directions increases of course with temperature ($\langle 110 \rangle$ in fcc: /33, 35-38/, $\langle 11\bar{2}0 \rangle$ in hcp: /30/) due to enhanced lattice vibration, but this has little influence on the yield.

There was confusion for some time about whether or not sputtering near the melting point would show an exponential yield increase and whether this

phenomenon could be attributed to thermal spikes /49,50/. Emission from surface areas which are intersected by such high density collision cascades was conceived as a sublimation/evaporation process which should therefore depend exponentially on temperature. This is, however, not the case. Even in situations where we can safely assume spike effects to determine emission, the angular distributions and their integrals remain only weakly dependent on bulk temperature /47/, Fig.7. Such a high-density cascade is met in heavy molecule ion bombardment: the molecule disintegrates at the first nuclear collision in the solid, the fragments deposit their energy in essentially the same cascade volume and one has energy densities where the majority of atoms is indeed in motion ($\equiv$ spike) /51,52/. Non-linearity between the numbers of impinging and ejected atoms is then observed.

Fig. 7: Temperature dependence of the differential yield of polycrystalline silver for 100 keV per atom Sb^+ bombardment. From HOFER et al. /47/.

Semiconductors behave differently from metals as regards radiation damage and sputtering. Their covalent binding prevents annealing of radiation damage below about 300°C. At this amorphous/crystalline transition the sputtering yield may vary by more than a factor of 2 /53/ and the angular distribution changes from a structureless form of Eq.2.2 to an anisotropic emission distribution /54/. Semiconductors therefore lend themselves particularly well to investigations of random matter and have been chosen in this sense for angular emission distribution studies /55-57/.

Anisotropic emission from monocrystals can be observed down to energies near the ejection threshold /20,58-60/, Fig.8. In this regime, none of the aforementioned mechanisms applies since the penetration depth of the projectiles is only 1 to 2 monolayers. Ejection is then accomplished only by direct projectile/target atom collisions as the higher generations of recoils have too little energy. In this respect, low-energy sputtering is similar to light-ion sputtering.

Light-ion sputtering, i.e. sputtering by hydrogen or helium isotopes, is mostly due to primary recoils. Owing to the small energy transfer by these projectiles, energy is deposited rather locally /61-63/. This results in a predominating influence of the projectile/target atom collision on the ejection process. Specific ejection kinematics, Fig.9, are to be considered

in interpretations of total (Y) and differential ($dY/d\Omega$, dY/dE) sputtering yields. For this reason the dependencies of these quantities on the projectile's mass, energy and incident angle are much stronger than in the cascade sputtering regime, Fig.10-13. Experimental as well as computer investigations have shown that it is the direct ejection of surface atoms by (back)scattered projectiles that is the preponderant ejection mechanism of light-ion sputtering.

Fig. 8: $\langle 110 \rangle$ emission distributions from an Au(100) surface bombarded by 50 eV inert gas ions. Ejection occurs due to backscattered projectiles. From VAN VEEN and FLUIT /60/.

Fig. 9: Collision kinematics of low-energy projectile impacts leading to ejection of surface atoms. a + b: Ejection of primary (b) and higher-order (a: secondary) recoils, c: Ejection by backscattered projectiles, d: Ejection of atoms recoiling at heavier constituents in the target.

2.2 Emission from Polycrystals

Despite the great interest single crystals had attracted since WEHNER's discovery in 1955, ejection distributions from polycrystalline solids continued to be the subject of experimental and theoretical investigations. This is mostly because the theories for light-ion, linear cascade and spike sputtering are all for random media. But there is also great interest in angular distributions in applied fields such as plasma-surface interaction and thin film production /55,65-68/.

In the case of sputtering by linear collision cascades and elastic collision spikes the emission distribution is largely independent of mass, energy and incident angle of the projectiles, see e.g. /55,56,67/ and HOFER's review in Ref.3, vol. III. They are all rotationally symmetric with respect to the surface normal and conform to

$$\frac{dY}{d\Omega}(\theta_0) \sim \cos^{\nu_0} \theta_0 \quad 1 \leq \nu_0 < 2, \quad (2.2)$$

where θ_0 is the polar angle of the out-going particle. Such behaviour is expected from the mechanism of (linear and non-linear) cascades and is reproduced by computer simulations /63,63a/.

In the low-energy regime of medium to heavy ion sputtering i.e. $m_1 > 4$, $E_1 < 1$ keV, the specific collisions shown in Fig.9 determine emission. At perpendicular projectile incidence, emission therefore takes place primarily at large polar angles (so-called "under-cosine" distributions) while at oblique incidence emission is mainly in the opposite, "specular", direction - similar to, but by far not as pronounced as for light-ion sputtering, Fig.11. As mentioned above, light-ion sputtering is primarily an effect of projectile/ target atom collision. Hence at perpendicular incidence ejection is due to backscattered projectiles. For this reason, the angular distributions are of the over-cosine type /66/, exactly opposite to angular distributions for heavier ions /54-58/. At oblique incidence the projectiles can eject surface atoms already on their way into the solid, which causes the dramatic increase of both the total, Fig.10b, and especially the differential yield in the specular direction, Fig.11. The direct ejection of surface atoms is also apparent in the energy distribution, where they cause a shift to higher energies and a hump at the high-energy tail of the spectrum, see Chap.3.

The contribution of all the ejection mechanisms based on a special constellation of the collision partners, namely

- ejection by primary recoils (Fig. 9a),
 - ejection of primary recoils (Fig. 9b,c), and
 - ejection by backscattered projectiles (Fig. 9c)
- becomes more and more a second-order effect as the collision cascade develops. This is primarily a matter of high enough projectile energy or, more properly, of high enough energy transfer to primary recoils.

Fig. 10: Dependence of the total yield on energy (a) and angle of incidence (b) of light-ion projectiles. The theoretical curves in (a) were calculated by LITTMARK and FEDDER /62/, assuming ejection to be entirely due to backscattered H^+ -ions. Fig. 10b is from BAY and BOHDANSKY /64/ and shows much stronger yield enhancement than is known in the linear cascade sputtering regime.

Fig. 11: Angular distribution of Ni sputtered by hydrogen ions of various incident angles. Preferential forward emission at grazing angle is due to primary recoil ejection (cf. Fig. 9b, 10b). From BAY et al. /65/.

2.3 Influence of Surface Topography

The development of surface structures on crystalline solids is a major problem in all sputtering investigations where fluences in excess of 10^{18} ions/cm² are applied. With polycrystalline targets the situation is worse because the stochastic orientation of the grains causes discontinuities in erosion speed at the grain boundaries. These discontinuities are likely to induce surface structures such as ridges and pyramids - in addition to the characteristic structures developing on the individual single crystalline grains. A polycrystalline surface subjected to intense particle irradiation will therefore be covered with arrays of differently oriented structures, mostly of the facet type, the orientation of the structures within the array (grain surface) often evincing astonishing regularity /69-71/.

Any deviation from a flat target surface must give rise to changes in yield and angular distribution, irrespective of the type of orientation of the structure. Because of the increase in yield caused by oblique incidence (cf. Fig. 10a)

$$Y(\theta_i) = Y(0) \cdot \cos^{-v_i}(\theta_i) \quad \text{for } 0 \lesssim \theta_i \lesssim 70^\circ \quad \frac{1}{2} \lesssim v_i \lesssim 3 \quad (2.3)$$

structured surfaces lead to enhanced emission; but recapture of ejected particles at these ridges, facets or cones may compensate this effect. LITTMARK and HOFER /72/ considered this problem theoretically in the cascade-sputtering regime and found the total yield in all cases of Eq.2.3 to be larger than for flat surfaces. Only in the case of steep, needle-like cone structures (incidence angle $\theta_i > 70^\circ$) will the recapture of released particles prevail and the yield therefore be smaller /73/.

Another noteworthy result was found for the angular distribution from polycrystals which develop facets. The emission distribution from such surfaces was found to be barely distinguishable from a cosine function, although the genuine distribution from a flat surface may be anything but of cosine shape. Surface structures appear to have a randomizing effect on the emission distribution. The genuine emission distribution may thus not be so well in keeping with isotropic theory as would appear from cosine-distributions obtained from structured surfaces. Careful electron microscopic control is thus a necessary accompaniment to angular distribution measurements on crystalline solids in order to guarantee that the observed distribution is not feigned by surface topography. If information on collision processes is the aim of the investigation, it is in any case preferable to conduct such investigations on amorphous solids such as semiconductors, which become amorphous when the irradiation is performed at moderate temperatures ($< 300^\circ\text{C}$) /55-57/.

3. INFORMATION FROM ENERGY DISTRIBUTIONS

The energy distribution of sputtered particles affords vital information on the mechanism of sputtering and the collision processes on which it is based. Thermal spike components, the theoretically predicted E^{-2} high-energy tail, focusing energies, and the refractive action of the surface barrier have been identified by dY/dE investigations. Owing to their experimental complexity, information on energy distributions came rather late

in the history of sputtering, and the number of dY/dE measurements is by far smaller than for $dY/d\Omega$, /74-92/ and Ref.3 Vol. III.

3.1 Sputtered Ions

Measurements of the energy distribution of sputtered ions are easier to perform than the analysis of neutrals, because problems associated with post-ionization for particle detection do not arise. Such ion spectra are of limited value in elucidating sputtering mechanisms, however, because particles undergo charge-changing processes during their passage through the surface. These processes are dwell-time, thus velocity dependent and therefore strongly influence the low-energy part of the spectrum. This effect may be described phenomenologically by

$$N^+(E)dE \sim N(E) \cdot P^+(E) dE \quad (3.1)$$

where $N(E)$ is the energy spectrum of sputtered neutrals, $N^+(E)$ that of sputtered ions, and $P^+(E)$ the probability that an ionized particle leaves the surface in this charge state /93-95/. Since $dP^+/dE > 0$, the measured ion distribution $N^+(E)$ differs from the energy distribution of neutrals in that the maximum is shifted to higher energies and the high energy tail is more pronounced. As will be discussed later, the same effect occurs with electronically excited (metastable) neutrals. Moreover, since ions constitute only a very small fraction ($< 10^{-3}$) of the flux of particles sputtered from clean metal surfaces, they may not be representative of the majority flux. Information on the main ejection mechanisms must, therefore, be deduced from spectra of neutral particles. There are, however, several cases where ion spectra are the only source of information, the most prominent examples being the energy distribution of sputtered clusters /92/ and that of the different components in alloys. Both fields are a domain of Secondary Ion Mass Spectrometry (SIMS).

3.2. Sputtered Neutrals

Energy analysis of sputtered neutral particles can most suitably be performed by

- time-of-flight (TOF) methods, and
- Doppler-shift methods using tuneable lasers.

The first, and also the most extensive, investigations of sputtered neutrals used the TOF technique. This is particularly true of the pioneering work of THOMPSON and co-workers. A high-speed spinning rotor was used for time-resolved registration of particles sputtered by a chopped ion beam /78/. The particle density condensed at the rotor rim reflects the velocity distribution of the sputtered flux; it was determined by autoradiography, but other trace analysis techniques can be used as well. Fig.12 is taken from this work.

The energy distribution of particles conforms to the relation (often referred to as the Thompson-formula)

$$N(E) \sim \frac{E}{(E + E_b)^3} \quad (3.2)$$

- The theoretical derivation of this relation is based on two assumptions:
- linear collision cascades; for such cascade recoils the energy distribution falls off with E^{-2} , see the overviews of ROBINSON and SIGMUND in Ref.3, Vol. I. This internal recoil spectrum is transformed into Eq.3.2 by virtue of a
 - planar surface barrier ($\sim E_b \cos^{-2}\theta$); this work-function type binding force leaves the momentum component parallel to the surface unaffected, while the normal component is reduced by an amount equivalent to the binding energy /78/.

The maximum of Eq.3.2 lies at half the sublimation energy ($\hat{E} = E_b/2$), a result which has been verified so often in the linear cascade regime that it became customary to characterize energy spectra by the purely thermodynamical quantity E_b . On the other hand, the confirmation of Eq.3.2 is an argument against the rotationally symmetric barrier used in the LS-model for anisotropic ejection, Chap.2.1. It is conceivable that these models can be reconciled.

Fig. 12: Energy distribution of sputtered Au atoms from a polycrystalline target. The mass of the projectiles was varied over such a large range that light-ion sputtering, linear cascade sputtering, and sputtering by collision spikes were covered. $\theta_i = 45^\circ$, $\theta_o = 75^\circ$. From AHMAD et al. /81/.

In reference to Fig.12, linear cascades are represented there by Ar^+ bombardment. There are deviations, however, for both substantially lighter (D^+) and heavier (Xe^+) projectiles. For light-ion sputtering neither the position of the maximum nor the high-energy tail conforms to predictions from linear cascade theory. This is explained by light-ion sputtering's being due to scattered or backscattered projectiles, see Chap.2. For this reason, the energy spectra also depend on the projectile's energy and incident angle /88,91/, Fig.13a,b; precisely this is not the case in the linear cascade regime /79-81/.

For heavy-ion bombardment, on the other hand, the high energy part of the spectrum in Fig.12 falls off with E^{-2} as is characteristic of linear cascades, but the low-energy portion of the spectrum is more pronounced. This is ascribed to collision spikes. Emission of atoms from spikes is conceived as a kind of evaporation from surface areas with temperatures of $3-10 \times 10^3$ K. In extreme cases temperatures up to 2×10^4 K have been reported /96/. There is still some controversy as to the magnitude of the partial spike yield deduced from unfolded energy spectra, as well as its dependence on target temperature. Neither the high spike yields nor the exceedingly large spike temperatures reported in /96/ have ever been reproduced. Contrary to the total yield, however, there seems to be some influence of the target temperature on the partial spike yield in energy spectra /79/.

Fig. 13: Velocity distribution of sputtered ground state atoms from polycrystalline Fe and Zr targets sputtered by light ions. The distributions are shifted towards higher energies in

- with increasing projectile energy owing to higher (primary) recoil energies. Average velocities are at 100 eV: 1.8 km/s, 500 eV: 4 km/s, 2500 eV: 6.2 km/s. From BAY and SCHWEER /91/.
- with increasing incident angle owing to direct ejection of surface atoms. Average velocities: 6.5 and 11.5 km/s. From BAY and BERRES /88/.

The results shown in Figs.13,14 were obtained by the Doppler-shift method, see also BETZ et al., this Study Institute. It is based on the shift of the excitation frequency by the velocity (Doppler effect) and is carried out by measuring the fluorescence yield as a function of the detuning of a (CW or pulsed) laser. The advantage of this method is that it can distinguish between atoms of different excitation, charge, and binding states. It thus allows discrimination of sputtered clusters (agglomerates of ejected atoms) which may falsify the low energy part of the spectrum, and it opens up a hitherto inaccessible field of spectroscopy, namely that of metastable neutrals, Fig.14.

3.3 Excitation and Charge State

During their egress from the surface the particles experience electronic transitions. The probability of excitation/ionization falls sharply with increasing excitation energy, whence ionization is a rare event ($< 10^{-3}$) compared to ejection as an excited neutral. Excited neutral particles either de-excite spontaneously, in which case they can be studied by spectroscopy of the light emitted immediately in front of the target surface, or they remain in metastable states. These excited metastable neutrals have recently attracted great interest because laser induced fluorescence has just come into the position of being able to determine their population and energy distribution. It was only in this decade that it was realized that excited neutrals may amount to up to 50 % of the sputtered neutral flux from clean metal surfaces /86/. The actual fraction depends on the projectile energy, and even more so on reactive gas coverage /84-90/. With oxygen exposure, for instance, the energy spectra change drastically: the ground state neutrals are reduced in intensity (a reduction factor of 50 was found for 15 keV $\text{Ar}^+ \rightarrow \text{Cr}$, and of 120 for 1 keV $\text{Ar}^+ \rightarrow \text{Ti}$) and show a deficiency in the low-energy part of the spectrum; the metastables show a shift of the spectra towards higher energies which increases with the excitation level, Fig. 14. In good agreement with observations on secondary ions, de-excitation or neutralization (see Chap.3.1) increases with the dwell time of exiting particles in the surface region. The survival probability $P(E)$ of an atom in a particular excitation state therefore falls with the velocity $v_{\perp}$ normal to the surface, a dependence of the form

$$P(E) \sim \exp \left(- \frac{\text{cons.}}{v_{\perp}} \right) \quad (3.3)$$

often being in at least qualitative agreement with observation. $P(E)$ can be generalized to include ionized states in Eq.3.1 as well.

Fig. 14: Velocity distribution of sputtered ground state and metastable excited state ($\Delta E = 0.6$ eV) neutrals from polycrystalline iron. The average velocity of the metastables is 19.6 km/s, a factor of 2 larger than the ground state neutrals. While the distribution of ground state atoms agrees with Eq. 3.2, there is no way to fit such a function with a thermodynamically reasonable binding energy. From SCHWEER and BAY /87/.

4. COLLECTIVE EMISSION

4.1 Cluster Emission

When around 1960 the first mass resolved flux measurements of positive and neutral particles were carried out, it became evident that a large fraction of particles is ejected as agglomerates of target atoms, clusters as they are called /98-101/. For many elements the intensity of cluster ions is so large that it can be utilized for production of composite ion beams which cannot otherwise be generated, e.g. Al_{17}^+ , V_{14}^+ , Cu_{11}^+ , U_5^+ , $(\text{V}_3\text{Nb}_4)^+$ /102,103/. Owing to this large intensity, clusters can also be used for chemical analysis of composite materials, since their stoichiometry correlates with that of the target (SIMS or SNMS analysis) /104-107/.

One should not under-estimate the fraction of bound species in the flux of sputtered particles. For secondary ions the number of atoms contained in agglomerates can easily amount up to 40 % of the charged flux. In the case shown in Fig. 15, for instance, summation over only the first three clusters ($n = 2,3,4$) yields about as many atoms ejected in clusters as in the atomic state. The key question, however, is whether information obtained with charged clusters can also be transferred to neutral clusters. Neutral diatomic fractions of 20 to 40 % can be deduced from published work on Cu and Ag /100, 105, 107/, and recent measurements of GNASER & HOFER suggest similarly high fractions for Ge. But it appears doubtful whether this result can be generalized /108/.

Fig. 15: Intensity ratio of clusters sputtered from polycrystalline copper and nickel. The appearance of oscillations in the abundance ratio for clusters with change in parity of the binding electrons (here Cu_n^+) reflects the importance of stability on cluster ejection. It should be noted that the number of atoms ejected in charged clusters is comparable in magnitude to the number of ejected atomic ions.
From RODRIGUEZ-MURCIA and BESKE /115/.

* Secondary Ion Mass Spectrometry
Sputtered Neutrals Mass Spectrometry

Cluster emission is one of the least understood fields in ion-solid interaction. Even the basic ejection mechanism is not established on a generally accepted basis. Two models exist which take quite opposite views: collective ejection, and statistical agglomeration of independently emitted atoms in the vacuum. Collective emission of surface atoms which constitute the cluster after the ejection event was the general consensus up to about 1975, when some measurements (on diatomic clusters), statistical calculations, and computer simulations suggested that clusters may also form by association above the surface /105,106,109-111/.

There is presently no decisive information obtainable from theory. Owing to the small energy of clusters /92/, the evolution of collision cascades has to be traced down to energies well below 10 eV. This is a regime where attractive forces also have to be included and the binary collision approximation is too crude. Plural particle interaction, however, has as yet been treated only by computer simulation. These calculations suffer from severe statistical problems due to the appreciable computation time required per emission event. Moreover, cluster stability after emission is an intricate issue /112-117/. Electronic, vibrational and rotational excitation may prevent the formation of a bound state. The importance of cluster stability is reflected impressively in the oscillating Cu_n^+ abundance distribution, Fig.15, which was first reported in sputtering by BLAISE & SLODZIAN (Cr^+ , Cu_n^+ , /113/) and HORTIG & MÜLLER (Ag_n^+ , /102/). The effect was known at that time from spark source mass spectrometry of group IV elements, see /111/ and references therein; also the explanation in terms of the parity of molecular orbitals is the same /112, 114/.

Owing to these complications in quantitative descriptions of cluster models one can do no more than rule out certain processes by general physical arguments. There is first the vanishingly small probability that clusters larger than dimers ($n > 2$) form by statistical association after the ejection event. Note that Fig.15 shows ejection probabilities of 10^{-2} up to $n = 9$. In a directed flux of atoms this can be accomplished only in correlated emission. This reduces the controversy to $n = 2$ clusters. For these, ejection from lattice sites further apart than next nearest neighbours can be ruled out because otherwise binding of the two atoms cannot be accomplished. Binding requires the relative kinetic energy to be smaller than the potential well. This rules out association of atoms which have not been nearest or next nearest neighbours in the solid. Similar to this argument which restricts the allowed area from where sputtered atoms may stem if they are to form a cluster, there is also a restriction which narrows down the perpendicular dimension: the last chance for the two atoms to dissipate excess energy is in the interaction region with the surface; this is again of the order of 5 Å. As these necessary conditions restrict the allowed volume to about $5 \times 5 \times 5 \text{ Å}^3$ it is very suggestive indeed to perceive the emission event as a collective one - even more so as there are also restrictions in time /92/: in order that particles can interact above the surface, the maximum time interval between two momentum transfer processes must not be larger than some 10^{-14} s . This is a very small fraction of the lifetime of a collision cascade.

To summarize, cluster emission thus appears to be an event at the very-low-energy stage of the cascade, where non-binary interactions favour simultaneous ($\Delta t < 10^{-13} \text{ s}$) knock-on processes near and in the surface, and where soft collisions upon egress from the surface reduce the relative

kinetic energy of the particles to be bound in the cluster or molecule. These cluster components need not necessarily stem from nearest neighbour sites in the lattice, although this becomes a more and more stringent condition with increasing cluster size. In all probability, nonlinear effects in high-density cascades near the surface will promote cluster emission.

4.2 Surface Craters and Sub-Cascades

An extreme case of non-linearity and collective emission has been reported by MERKLE & JÄGER /118/. In electron-microscopy investigations of defect structures created by heavy-ion bombarded Au MERKLE observed - in addition to collapsed depleted zones in the bulk - surface craters of about 50 Å in diameter. About 10^3 atoms have to be removed to form such a crater. The number of these craters increased sharply with energy and was particularly pronounced for molecular ion (Bi_2^+) bombardment Fig.16. At an energy of 100 keV the material removed just from these craters - there are presumably many more of sub-microscopic size - had reached the yield value calculated from linear cascades. This is the same energy range where BAY et al. /119/ have measured enhanced Au-selfsputtering yields which they have attributed to collision spikes. MERKLE follows this explanation but points out that it is not so much the average (linear) cascade size which determines high-energy (> 100 keV) sputtering, but the individual sub-cascade as long as it is generated only near enough to the surface. These sub-cascades are the zones which constitute the spike, and their distribution in space must be known in order to allow a more accurate calculation of sputtering yields. This problem is coupled to the often addressed fluctuations in energy deposition in individual cascades; for further details in connection with cluster emission see also /120/.

Fig. 16: Energy dependence of the total (Δ) and partial ($\circ$) sputtering yield of polycrystalline gold due to Au^+ , and Bi^+ , Bi_2^+ bombardment, respectively. From MERKLE & JÄGER /118/.

4.3 Microparticle and "Chunk" Emission

Microparticle emission had already been observed in the first erosion investigations of cathodes in glow discharges. PLOCKER /10/ reported luminous objects leaving the cathode without any influence of electric or magnetic fields on their trajectory. HITTORF /9/ gave an explanation in terms of cone formation: after prolonged bombardment of Al-cathodes he observed needle or hair-like structures which, owing to their reduced thermal contact to the bulk of the cathode, start melting at their tips and thereby emit macroscopic particles. Such an explanation can also be found in recent work on exfoliation and blistering, see SCHERZER's review in Ref.3, Vol.II.

Emission of μm -sized particles containing up to 10^{10} atoms was recently also found in neutron sputtering, where it caused the sputtering yields to exceed the physically reasonable values ($\sim 10^{-5}$ atoms/neutron) by orders of magnitude /121/. The concern which this high erosion caused in the thermonuclear fusion community triggered off intensive research in several laboratories. The final consensus was that chunk emission in neutron sputtering is due to loosely bound particles on "technical surfaces" /122/.

5. SUMMARY

Sputtering of elemental metals and semiconductors is well understood in the regimes of specific knock-on ejection, i.e. light-ion as well as near-threshold sputtering, and linear collision cascades. Theory is often in remarkably good quantitative agreement with experiment, in spite of large uncertainties in the interaction potential at those energies which dominate in the emission spectrum.

The lack of knowledge of interatomic forces, in both the repulsive and the attractive regions, is the main obstacle to a better understanding of the emission and stability of clusters. Their contribution to total ejection is not negligible.

Understanding of sputtering by collision spikes also suffers from uncertainties in the low-energy interaction region, but the main problem to solve in this regime is the energy transport across the spike/solid interface as this determines the evolution of the spike in space and time as well as energy confinement in the cascade volume. Sputtering by spikes is also experimentally not satisfactorily established; it is still not clear to what extent the low-energy part of energy spectra is influenced by non-linear effects, the lattice temperature, and clusters.

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"In erster Linie haben wir die Zerstäubung als Verdampfung zu betrachten und auf die hohe Temperatur an der Oberfläche der Kathode zurückzuführen. Es können die Metallmoleküle da, wo positive Ionen auftreffen, infolge von deren riesiger kinetischer Energie für kurze Zeit unmittelbar nach dem Auftreffen eine sehr hohe Temperatur von den positiven Ionen übernehmen, infolge davon in den Gasraum hineinverdampfen ..."
"We must regard sputtering primarily as evaporation caused by the high temperature at the surface of the cathode. Where the positive ions strike, the metal molecules can acquire from them, as a result of their huge kinetic energy, a very high temperature which persists for a short time directly after the impact; the metal particles consequently evaporate into the vacuum ..." p. 434
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"Ein Atomstrahl (Kanalstrahl) besitzt eine große kinetische Energie; beim Auftreffen auf ein Atom an der Oberfläche eines festen oder flüssigen Körpers kann er an dieses einen Teil seiner kinetischen Energie durch Stoß abgeben, mag er hierbei reflektiert werden oder nicht. Indem das getroffene Atom eine Geschwindigkeitskomponente in der Richtung des auftreffenden Atomstrahls von diesem übernimmt, wird es in gewissem Sinne selbst zu einem geladenen oder ungeladenen Strahle und kann, indem es auf seinem Wege auf ein anderes Atom trifft, an diesem eine Reflexion erfahren: und erhält es hierbei eine Geschwindigkeitskomponente senkrecht zur Oberfläche nach außen, so kann es aus dieser heraus in den Gasraum übertreten ..."
"An atomic ray (canal ray) possesses a large kinetic energy; during impact with an atom on the surface of a solid or fluid body, it can give up a part of its kinetic energy to the atom in the collision, whether or not thereby undergoing reflection. The atom struck acquires a component of velocity in the direction of the incident atomic beam, it will itself in a sense become a charged or uncharged ray and can experience reflection by striking another atom in its path; should it thus acquire a velocity component outwards normal to the surface, it can exit from the surface into the vacuum ..." p. 754

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