Sputtering of Molecules and Clusters:
Basic Experiments and Theory

By Herbert M. Urbassek

Fachbereich Physik, Universität, PF 3049

D–67653 Kaiserslautern, Germany

and

Wolfgang O. Hofer

Forschungszentrum Jülich

Institut für Plasmaphysik, EURATOM Association

D–52425 Jülich, Germany

Synopsis

A review is given of experimental and theoretical results on the sputtering of clusters obtained after the last Symposium on Sputtering (1986). We shall restrict ourselves mostly to collisional emission from electrically conducting, elemental solids upon energetic particle bombardment.

After a short historical survey, the size distributions of sputtered clusters will be presented and compared with those of other surface emission phenomena such as (thermal and laser-induced) sublimation and field evaporation.

The interpretation and in particular the pronounced dependence of the size distributions on the charge state are still controversially discussed in the literature. Also, the extent to which cluster fragmentation influences experimentally determinable emission distributions is not yet finally settled. The key quantities here are the cluster binding and ionization energy and the internal kinetic energy distribution in the cluster. These quantities are only poorly known. But there are also experimental difficulties to overcome, such as the effect of post-ionization on cluster stability, the comparatively long flight time in the particle spectrometer, and discrimination in heavy-particle detection.

Cluster fragmentation also has a direct bearing on one of the fundamental questions in sputtering, namely the fraction of atoms in the sputtered flux that is ejected in a bound state.

Kinetic energy distributions display an E^{-2} decay at high emission energies E for a wide class of sputtered molecules. This applies if strongly bound molecules are emitted which are only weakly bound to their surroundings. Such a soft decay is taken as evidence that the molecule has been emitted by a single strong collision of a recoil atom in the collision cascade set up by the bombarding particle. This feature is often observed in the emission of molecular reaction products in reactive ion etching.

The spectra of dimers sputtered from elemental metals, on the other hand, show a steeper decay with emission energy, which has been measured to lie between an E^{-3} and an E^{-5} asymptotic by different researchers. Such a steep fall-off is indicative of more than one collision being active

in emitting the cluster. In this area, recent molecular-dynamics computer simulation experiments have been performed with appropriate metallic many-body potentials and good statistics to give more details of the emission mechanism.

1   Introduction and Historical Survey

When a solid surface is bombarded by energetic atoms or ions, particles are emitted (sputtered) from the surface. In the sputtered flux, not only atoms and monatomic ions are found, but also polyatomic molecules and clusters.[1] The sputtering of molecules and clusters is a ubiquitous phenomenon. It has been found under ion bombardment of metals, semiconductors, and insulators; for elemental targets, alloys, and compounds; for molecular crystals, bio-organic, and polymeric materials.

Clusters containing an impressingly high number of atoms have been found in sputtering experiments. Fig. 1 gives an example for a metallic target, both for charged and neutral sputtered clusters.

The sputtering of clusters is interesting in itself: While the sputtering of atoms is for most systems a consequence of the momentum imparted to a (near-) surface atom in the collision cascade set up by the bombarding ion (Behrisch, 1981; Behrisch, 1983; Behrisch & Wittmaack, 1991), the emission of large clusters from strongly bonded materials has been tentatively connected to the collective or correlated emission of several atomic species (Hofer, 1980; Merkle & Jäger, 1981; Andersen, 1989; Hofer, 1991). Thus, the mere existence of large clusters in sputtering is certainly one of the important open problems in sputtering physics.

The sputtering of clusters has also found a number of interesting applications: The significance of the ion-bombardment induced desorption of organic and biomolecules has been discussed elsewhere in this Volume. Cluster emission is invariably observed in secondary ion (SIMS) and sputtered neutral mass spectrometry (SNMS) experiments and has been used in connection with surface analysis (Schou & Hofer, 1982; Oechsner, 1990; Downey et al., 1992). When surfaces are bombarded by reactive ions or by inert ions in a reactive environment, the total sputter rate can be increased, since molecular, more volatile, reaction products are more easily emitted than the unreacted material. This application of molecular sputtering is used as reactive ion etching (RIE) (Oostra & de Vries, 1987). Finally, cluster sputtering has been used as a cluster source. Since sputtered clusters are internally quite hot, this application has been comparatively rare (Thum & Hofer,

---

[1]The choice of words is somewhat fuzzy in the literature. We shall use the term 'cluster' in a broad sense to mean any aggregation of atoms. By 'molecules' we mean more specifically those strongly bonded atomic aggregations which already existed in or on the solid before bombardment, such as in molecular crystals, or which are formed under ion bombardment by chemical reactions, such as in reactive ion etching.

1979; Magnera et al., 1985; Begemann et al., 1986; Fayet et al., 1986).

The emission of clusters from solid surfaces was discovered about 50 years ago (Hahn et al., 1942; Mattauch et al., 1943). This was in an RF-spark between carbon electrodes, and hence clusters originated from sublimation. In the fifties, Honig (1953; 1954) continued this work and performed fundamental research on thermal emission from group IV elements. Later he (Honig, 1958), Krohn (1962), and others turned to sputtering as a source of ions for mass spectrometry, and their work must be considered as the first detection of the phenomenon of cluster sputtering (Hofer, 1991). Of course, in these measurements only cluster ions were detected.

Several researchers tried to detect neutral particles. Post-ionization with electron beams was the preferred method then. With the notable exception of Woodyard & Cooper (1964) this failed because of background problems caused by the residual gas. Woodyard & Cooper found a surprisingly high fraction of sputtered clusters (dimers and trimers) in the flux of neutral particles. This irritating uncertainty on one of the fundamental questions in sputtering, namely the fraction of bound particles in the sputtered flux, persisted for the next two decades and is only now in the process of being clarified.

Mass distributions[2] of cluster ions were first reported by Blaise & Slodzian (1968) and Hortig & Müller (1969). With the broad use of the SIMS analysis technique, such distributions became available for many elements and multicomponent targets. When assuming that the charged and neutral distributions follow a similar behavior, all these results pointed towards an appreciable (20-30%, in some cases even more) bound particle flux. This picture changed somewhat when Gerhard & Oechsner (1975) published the first neutral-cluster intensity ratios, i.e., dimer-to-atom and trimer-to-atom ratios. Although this investigation was carried out on a much broader experimental and theoretical basis than that of Woodyard & Cooper (1964), the choice of experimental parameters as well as unknown instrumental influences on cluster dissociation prevented an assessment of bound particle fluxes in the collision-cascade regime. The picture changed when Gnaser & Hofer (1989) found in a direct-comparison experiment the mass distributions of neutral clusters to fall off much more steeply with cluster size than for charged clusters. This holds down to cluster/atom intensity ratios of about 10^{-4}, thus covering the vast majority of the flux of sputtered particles. Still lower intensity ratios became accessible with the laser-ionization technique (Coon et al., 1991; Wucher et al., 1993). At this low level, the emission processes are hardly representative of the general phenomenon of sputtering but they are highly interesting in the elucidation

---

[2]Following a general practice, we use the terms mass, abundance, and cluster-size distribution synonymously. (As-measured) mass spectra should, ideally speaking, be corrected for instrumental effects in order to yield mass distributions. This is only seldomly done, however.
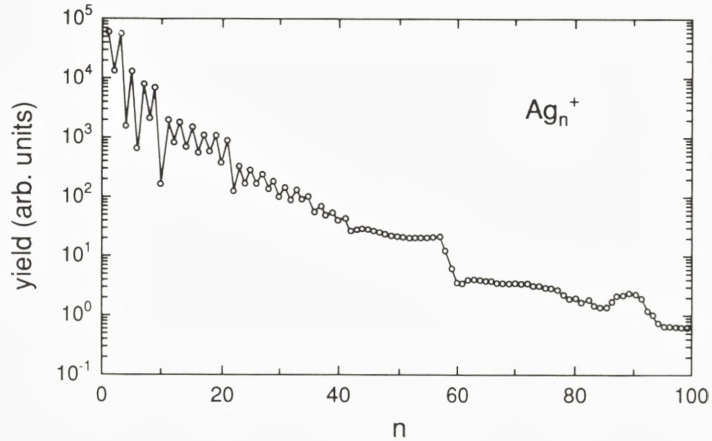
Figure 1a. Experimental data on sputtered Ag cluster abundance distributions. Ionized clusters Ag_n^+ sputtered by 10 keV Xe^+ ions (Katakuse et al., 1985). The intensity drops at Ag_9^+, Ag_{21}^+, and Ag_{41}^+ should be noted. They are associated with 'magic' numbers of binding electrons, for which jellium-type calculations yield binding energy maxima for 8, 20, and 40, respectively, $5s$ electrons.

of cascade-fluctuation effects as well as for specific cluster-emission events. Information available from cluster-size distributions will constitute a major part of this review.

Cluster abundance distributions are not stable during the first 10 μs or so after the clusters' genesis. The importance of fragmentation has been first shown by Ens et al. (1983) for ionically bound clusters, and by Dzhemilev et al. (1985) and Begemann et al. (1986) in the case of metal clusters. These studies showed that the cluster abundance distribution strongly changed its characteristics with the time spent after cluster formation, cf. fig. 2. The consequence of cluster fragmentation is that practically all mass spectra measured so far do not represent the emission distribution in sputtering. Rather they come near to the stationary distribution, depending strongly on the experimental technique employed for mass analysis.

In the early seventies, a number of groups started measurements of the energy spectra of charged clusters (Dennis & MacDonald, 1972; Staudenmaier, 1972; Herzog et al., 1973). This work was followed by Bernhardt et al. (1976) who were the first to monitor neutral dimer kinetic energy distributions. It was only recently that kinetic energy distributions of larger neutral clusters be measured (Brizzolara & Cooper, 1989; Coon et al., 1991; Wucher et al., 1993).

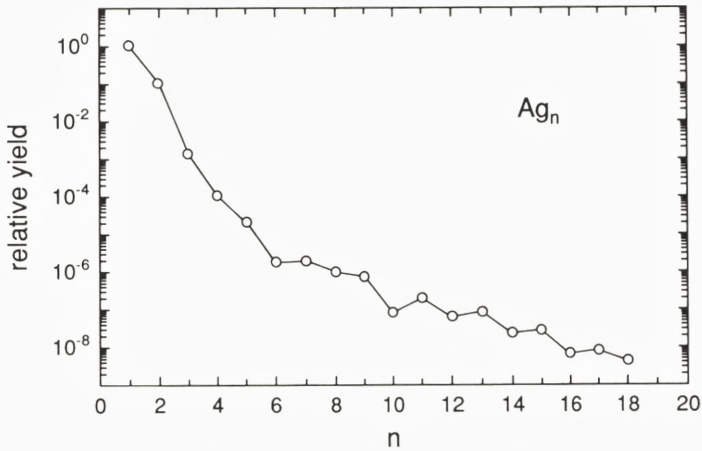Information on the internal energy distribution of sputtered clusters has been

Figure 1b. Same as fig. 1a for neutral clusters Ag_n sputtered by $5\,keV\ Ar^+$ ions (Wucher et al., 1993).

determined only for a small number of systems. Apart from the early work of Thomas & Efstathiou (1984) and Snowdon & Heiland (1984) on molecules emitted from N-bombarded Si, and of de Jonge et al. (1986a) on sulphur, the experiments by Fayet et al. (1986) on sputtered alkali dimers are particularly noteworthy.

In parallel with these experiments, theoretical models were developed and computer simulations were performed with the aim of clarifying the mechanisms underlying cluster emission. Already quite early, the two dominant models describing cluster emission were developed: The idea that clusters may be 'emitted as such' from the ion-bombarded surface seems to go back to Honig's work (1958), cf. also Staudenmaier (1972). The 'association' of individually energized[3] recoils was formulated by Gerhard (1975) and Können et al. (1974). Since then, the controversy about these two models has accompanied the discussion. As we shall note at the end of the present review, this discussion is based more on lack of care in the proper choice of words than on physically realistic and experimentally discernible distinctions.

Computer simulation in this field was pioneered by the work of Harrison & Delaplain (1976). While early studies used pair potentials even for metallic targets (Harrison, 1988), modern simulations employ many-body potentials, which are believed to be more realistic. Also, in order to obtain a representative picture of

---

[3]We are intentionally avoiding the term 'sputtered' or 'ejected' for particles which are still on their way out of the interaction region of the solid.
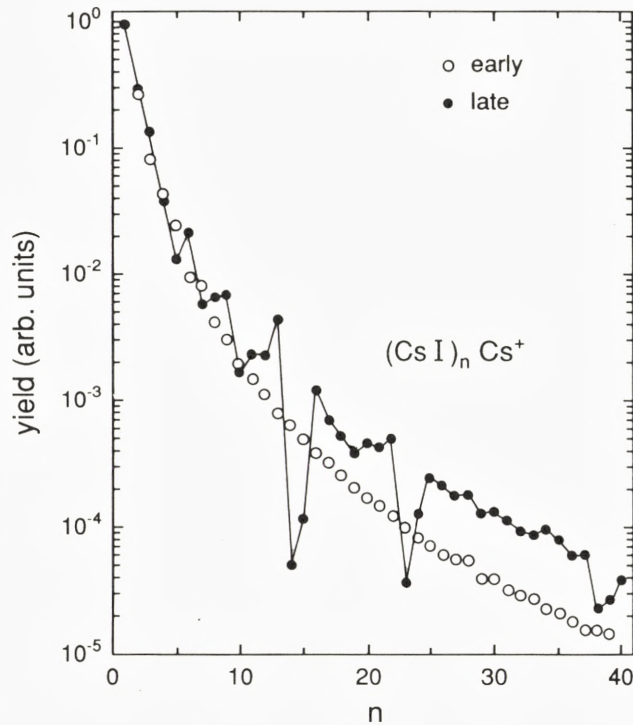
Figure 2. Relative yield of $(CsI)_n Cs^+$ clusters sputtered by $3.6\,keV\ Xe^+$ ions from a CsI target. Early (late) distribution taken at $0.17\,\mu s$ ($750\,\mu s$) after ion bombardment; these times apply for an $n = 13$ cluster. Data taken from Ens et al. (1983).

the emission mechanism, a large number of ion impact and cluster emission events, of the order of 10^3 or more, are simulated (Wucher & Garrison, 1992a).

In our review, we shall concentrate on the work done in the field of sputtering of clusters and molecules after the Symposium on Sputtering in Spitz, Austria, 1986 (Betz et al., 1987). As the historical survey just given shows, considerable work had been performed before this date; it was reviewed by Kelly (1984), Oechsner (1985), de Vries (1987), Urbassek (1987), and Hofer (1986; 1991). In the present review, we shall restrict ourselves mostly to collisional emission from electrically conducting, elemental solids upon energetic particle bombardment. Sputtering of molecules from more complex materials, such as (bio-) organic solids, polymers, or cryogenic ices, have been covered elsewhere in this Volume (Reimann, 1993). We shall focus on situations in which the bombarding ion establishes a linear collision cascade (Sigmund, 1981). Ion bombardment induced spikes will not be considered

here, even though experimentally observable emission of large chunks of matter, as reviewed by Hofer (1991), and described with recent references by Baranov et al. (1992), is often assumed to occur in a spike scenario.

2   Cluster-Size Distributions

Fig. 1 shows measured cluster abundance distributions for a metallic target, both for charged and neutral sputtered clusters. For both cases, a strong overall decay of the cluster abundance with the number n of atoms contained in the cluster can be observed. This reflects the cluster-formation probability which decreases with increasing number of atoms. In a direct comparison of the abundance distribution of charged and neutral clusters sputtered under identical conditions from the same element, two differences between ionized and neutral clusters became apparent (Gnaser & Hofer, 1989):

(i) neutral clusters show a stronger decay with atom number n than charged clusters;

(ii) the conspicuous even-odd alternations of charged clusters of monovalent elements are absent in the distribution of the neutrals.

Both findings were confirmed and extended by Franzreb et al. (1991a).

Cluster abundance distributions have been interpreted from the very beginning in terms of the clusters' electronic structures (Joyes, 1971; Leleyter & Joyes, 1973; Rodriguez-Murcia & Beske, 1978; Joyes & Sudraud, 1985). Because of spin-pairing of binding electrons, clusters with an even number of valence electrons possess an increased stability, which is enhanced both with respect to fragmentation and ionization. Thus, clusters containing an even number of binding electrons show both an enhanced dissociation energy and a larger ionization potential. It became customary to interpret cluster abundance in terms of stability against fragmentation/dissociation. This was probably influenced by the success with covalently bonded clusters (Dörnenburg et al., 1961), where indeed the binding energy controls the mass distribution – of course, apart from the kinetics of cluster formation which prescribes a monotonically decreasing dependency. However, it is also true that there remained a latent awareness that the ionization energy, too, must be an important parameter for the understanding of abundance distributions, in particular for charged clusters (Leleyter & Joyes, 1973). This issue was taken up and emphasized recently (Franzreb et al., 1991a).

Fig. 3 displays quantum-chemical data for the variation of the binding energy of a cluster with the number of atoms it contains. The binding energy of a charged cluster is definitely higher than that of a neutral cluster. This applies
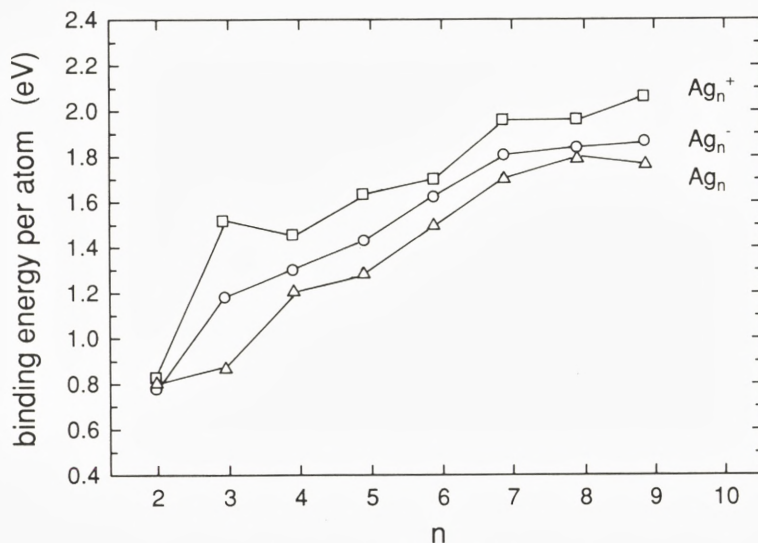
Figure 3. Binding energy per atom of charged and neutral Ag clusters. Quantum-chemical calculations due to Bonacic-Koutecky et al. (1993a,b). For comparison: Bulk sublimation energy of Ag: $2.96\,\text{eV}$.

both if iso-nucleonic clusters (vertical lines) and iso-electronic clusters (e. g., $Ag_4 \rightarrow Ag_5{}^+$) are compared. Interestingly, these calculated binding energies do not display the odd-even alternations as pronouncedly as earlier, simplified calculations where an oscillatory structure in the dependence of the binding energy was intimated. Binding-energy considerations, therefore, cannot explain the odd-even oscillations in the mass spectra of charged clusters of monovalent metals. The monotonically decreasing neutral-cluster intensities, on the other hand, are in keeping with calculated binding energies.

The question why the abundance distribution of charged clusters alternates while that of neutral clusters does not,[4] appears to be connected to the behaviour of the ionization energy, rather than to the binding energy (Franzreb et al., 1991a): As the experimental data plotted in fig. 4 show, the ionization energy of clusters indeed shows these oscillations. The comparison of charged and neutral cluster abundancies hence motivates the following assumption about the ejection process: First the cluster is formed in the neutral state. In a second step it is ionized while it leaves the interaction range with the surface.

[4]The origin of the slight alternations visible in fig. 1b for neutral clusters is not clear; it may, in fact simply stem from the detection method, viz. single-photon ionization (Wucher, 1993).
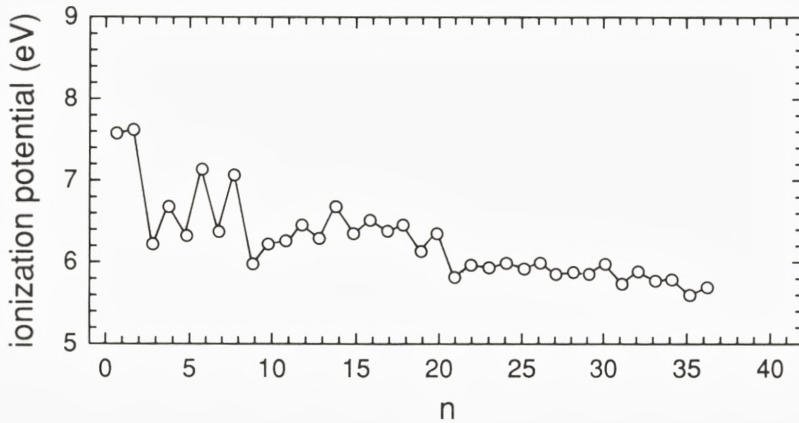
Figure 4. Ionization potential of neutral Ag clusters, measured by electron impact ionization (Jackschath et al., 1992). For comparison: Work function of Ag: 4.26 eV.

This sequence of processes is the same as in the ionization of clusters stemming from gas-agglomeration sources. Such cluster sources are in frequent use in cluster research: Material of which clusters are to form is evaporated into an inert-gas cell, where agglomeration takes place. Collisions with inert-gas atoms mediate the agglomeration and cool the clusters by dissipating the heat of condensation. Further cooling can be achieved by adiabatic expansion in a supersonic nozzle. For such a system, Powers et al. (1983) reported a smooth, monotonically decreasing size distribution of neutral Cu_n clusters. Characteristic odd-even intensity alternations appeared only in the cluster-ion spectra. For this to occur, it was important to carry out the ionization with energies near the ionization threshold; only then is the process selective and allows intensity modulation according to the ionization potential, cf. fig. 4. The intensity oscillations in the mass spectra of cluster ions are, therefore, a kind of artifact caused by ionization of neutral clusters in the threshold region of the ionization cross section.

In the above gas-agglomeration experiments, cluster formation and ionization are well separated in space and time. In sputtering, the situation is more complex: Firstly, the knock-on collision, cluster formation, and ionization all take place within 5 Å from the surface atomic layer. There is, thus, no clear separation of cluster formation and ionization. For this reason, ionization takes place long before the clusters had time to dispense of their excess energy. In surface emission of clusters, hot clusters are ionized. Remarkably, however, ionization makes for a stabilization of the cluster, cf. fig. 4.

The cluster ionization process directly depends on the bonding and electronic structure of the cluster: For metallic targets, often the electron tunneling model (Yu, 1991) of atomic ion formation in sputtering is extended to cluster-ion emission (Franzreb et al., 1991a; Makarenko et al., 1991); this implies, as we discussed above, that the cluster formation and ionization processes can be separated in time from one another. Similar considerations also apply to negative-ion formation (Abdullaeva et al., 1991; Wada et al., 1991). Other mechanisms dominate the sputtering of non-metallics, and in particular of compound targets, where the charge state of the cluster and its emission mechanism may be closely connected (Yu, 1981; Yu, 1982; Klimovskii, 1987).

Theoretical results on the mass distribution of sputtered clusters are not readily available. Computer simulation does not provide sufficient statistics to study representative ensembles of clusters containing more than 2 or 3 atoms. Analytical models hence use statistical, bond-counting considerations (Dunlap, 1982; Dunlap et al., 1983) which invariably lead to an exponential decay of cluster abundance with mass. A collective model of large cluster formation predicts a slower decay if clusters are formed in an equilibrium process in the vicinity of the critical point of the liquid-gas phase transition (Urbassek, 1989). A power-like dependence has indeed been observed in charged clusters sputtered from ion-bombarded rare-gas solids (Orth et al., 1981; Jonkman & Michl, 1981; Urbassek, 1988b).

Cluster abundance distributions from metallic targets have for a long time been believed to obey the dependence $Y_n \propto Y^n$ with cluster size n (Gerhard, 1975). Such a relationship stems from statistical considerations, which imply that clusters originate from a fixed 'active' area, viz. the intersection of the collision cascade with the target surface. Recently, Gnaser & Oechsner (1991; 1993) and Wurz et al. (1991) checked this law by varying the total yield Y via the bombarding energy of the ions inducing sputtering and measuring the emission-angle integrated dimer and trimer yields. For bombarding energies below 1 keV they verified the law for a variety of metals and alloys. However, recent experiments (Franzreb et al., 1991b) and computer simulations (Wucher & Garrison, 1992b) cast doubt on its validity for higher bombarding energy. Note, however, that by varying the bombarding energy, also the area is changed, from which particles are emitted, and hence the above law, $Y_n \propto Y^n$, need in principle not be fulfilled. An experiment using equi-velocity (light) clusters as projectiles might be better suited to test this law (Sigmund, 1993).

Finally, we note that it has been known for a long time that the sputtering of clusters is due to the effect of a single ion impact, rather than to the combined effect of several ions; a notable exception will occur for (heavy) cluster bombardment. It has also been noted frequently that there exist considerable statistical fluctuations in the collision cascades and hence in the sputtering yield. This must have a major

importance on the cluster abundance.[5] As for instance Cooper & Hamed (1984) note, dimer emission may be observed in situations where the total average sputter yield is substantially below 1; nevertheless, a non-vanishing probability for the emission of two atoms from the same collision cascade must have existed. Or, as Wittmaack (1979) observed, $Si_n{}^+$ clusters up to $n = 8$ appear under average yield conditions of $Y \cong 1$ atom/ion. One might indeed expect that the cluster size distribution reflects the fluctuations of the individual collision cascades. The average yield or an average of the deposited energy in the near-surface region are of little help when the observable shows such a large statistical variance as that of the cluster-size distribution.

Hence, at low bombarding energies, data on the monomer and dimer yield may give direct experimental information on the statistics of the sputter yield. A complete theoretical prediction of cluster abundancies taking these fluctuations into account and going beyond Gerhard (1975) does not yet exist.

2.1   Odd-even Alternations, Magic Numbers

Alternating cluster ion intensities are a general feature of clusters composed of atoms with an odd number of valence electrons. Although the effect is best documented for monovalent elements such as the alkali and noble metals, it is evident also for group III elements such as Al. In sputtering of alloys, the odd-electron atom imposes the alternations on the abundance distribution of composite cluster ions (Joyes et al., 1986).

The alternation effect exists both for negative and positive cluster ions, and in the latter case as well for multiply charged clusters (Joyes & Sudraud, 1985). In all cases, the intensity maxima correspond to an even number of valence electrons in the cluster.

It is interesting to note that alternating cluster ion intensities appear to be a general feature of clusters originating from surfaces of (metallic) solids or liquids. The effect is by no means confined to sputter ejection. It is well discernible in the charged flux of particles from a liquid-metal ion source (LMIS) (Joyes & Sudraud, 1985; Bhaskar et al., 1987), and also in the cluster-ion abundance from laser irradiated solids (Fürstenau & Hillenkamp, 1981). Interesting in this context is also the fact that the alternation effect for metal clusters decreases with increasing laser power, i.e., when cluster formation shifts from the surface into the adiabatically expanding vapour cloud in front of the target. Here, another cluster formation and ionization mechanism takes over. This corresponds to neutral cluster formation in

---

[5]This has often been noted in the literature (Staudenmaier, 1972; Staudenmaier, 1973; Sigmund, 1977; Wittmaack, 1979; Winograd et al., 1978; Winograd et al., 1979; Sigmund, 1987; Eckstein, 1988; Conrad & Urbassek, 1990).

supersonic nozzle beams.

The phenomenon of magic numbers in abundance distributions has recently attracted much attention in cluster research. Similar to atomic nuclei, agglomerates containing a certain ('magic') number of constituents manifest themselves by an enhanced abundance compared to their neighboring species. This effect is generally explained in terms of increased stability, i.e. binding energy. As the bulk of these magic-number studies of clusters has been carried out by non-surface emission methods, there is little uncertainty in this interpretation caused by interference from the ionization process. The origin of the enhanced stability may be quite different in differently bound clusters, however: While in ionically bound clusters the geometric ('crystal-') structure is assumed to play an important role (Campana et al., 1981), the binding in clusters composed of metal atoms is purely electronic. Therefore, the magic numbers of $n = (2), 8, 20, 40, \ldots$ given for metal clusters refer to the number of binding electrons. The number of atomic constituents thus varies with the charge state of the cluster (e. g. Ag_9^+, Ag_8, Ag_7^- for the magic number 8 in figs. 1a and 3). We note in passing that these agglomerates are still far from evincing bulk metallic characteristics. This can be seen, for instance, in the differences to the bulk sublimation energy and the work function given in figs. 3 and 4, respectively.

Magic numbers can readily be identified in sputtered cluster-ion abundance distributions, cf. fig. 1a. Actually, the fact that sputtered clusters have a rather high internal energy and are thus subject to larger fragmentation rates (see below), increases the intensity contrast between loosely and tightly bound clusters in the mass spectra; cold clusters would not reflect their differences in binding energy in mass spectra. In general, however, the enhanced internal energy of sputtered clusters is considered as a disadvantage in cluster research. It also limits the applicability of sputtered-cluster sources in this field. For the phenomenon of sputtering, magic-number clusters have hardly any significance due to their vanishingly small fraction in the total flux of ejected particles.

No magic number characteristics have as yet been detected in the flux of sputtered neutral clusters. As with the odd/even alternations, the spectrum of neutral clusters is poorer in information than that of the charged species. This may again be a consequence of the close coupling of cluster formation and ionization in emission from surfaces. In nozzle-type experiments, by contrast, identification of magic-number clusters both in the neutral and the charged state seems to be the role.[6]

---

[6]The actual measurement always requires ionized clusters. The difference to sputtered clusters is that post-ionization is performed here on cool clusters. It would be interesting to carry out on sputtered clusters a post-ionization experiment at a cluster lifetime $> 100\,\mu s$, i.e., after fragmentation has left the clusters at lower internal energy.

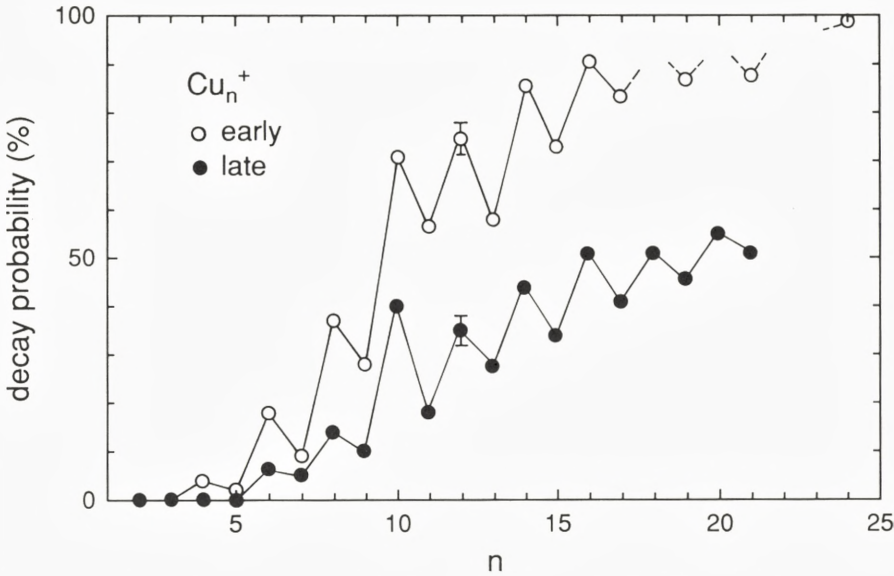Figure 5. Decay probability of $Cu_n{}^+$ clusters sputtered by 21 keV Xe^+ bombardment. Decay is observed on two groups of clusters ('early' and 'late') which differ by the time after which decay is monitored. Early clusters decay with considerably higher probability than late clusters. Data taken from Begemann et al. (1986).

2.2 Fragmentation

Sputtered clusters are not stable right after the ejection process. Collisional ejection leaves the agglomerates with a high amount of internal energy. This causes fragmentation during a time span of $10\,\mu s$ or more after the clusters' generation. The mass spectra change with time during this period, as was first demonstrated by Ens et al. (1983) for ionically bound clusters, cf. fig. 2. Here it was shown that the cluster abundance distribution strongly changed its characteristics with the time spent after cluster formation. While the 'early' distribution shows no alternations, these do form during the flight (cf. fig. 2). Apparently, characteristic structures in such mass spectra evolve as the clusters approach their stability distribution.

For metallic systems, cluster fragmentation has been investigated mainly at the Academy of Science in Tashkent by Dzhemilev & Verkhoturov (1985) and Dzhemilev et al. (1987; 1990; 1991) and at the University of Bielefeld by Begemann et al. (1986; 1986; 1987). Fig. 5 represents results obtained with $Cu_n{}^+$ clusters by the latter group. The two curves shown therein correspond to time intervals opened after different times after sputter ejection. The 'early' time interval is opened

typically 50 ns after ejection, the 'late' at about 500 ns. The recording time is given by the drift time of the clusters in the time-of-flight (TOF) spectrometer. It is more than an order of magnitude longer than the 'late' delay time. 'Late' and 'early' mass spectra thus differ by the amount of clusters which have undergone fragmentation before entering the spectrometer. The decay probability plotted on the ordinate is the fraction of clusters of a given size that has undergone fragmentation during the flight through the spectrometer. In short, the main findings of these investigations, as far as they are relevant for sputtering, are:

- Small clusters attain their stability configuration quickly. After some 100 ns, no Cu_n^+ clusters up to n = 5 but a small fraction of quadrumers are subject to decay. During this time, the clusters have moved no farther than $10 - 100 \, \mu m$ from the surface; conventional mass spectrometers will all yield the same mass distribution. If it is allowed to transfer these results to neutral clusters, it can be stated that the majority of the sputtered flux, i.e., the flux of $n = 1 - 5$ species, is stable against fragmentation once it has cleared off the surface.

- The main form of fragmentation is the emission of neutral atoms. This is the most effective way of reducing the internal energy in the cluster. Klots (1985; 1991) used such data to shed light on the fragmentation kinetics and to correlate it with thermodynamic cluster properties. While his calculations put the emphasis on cluster stability considerations derived from binding energies, his approach could be broadened to include the structure visible in cluster ionization potentials.

- The fragmentation pattern shows odd-even oscillations for monovalent metals. Cluster ions with an even number of valence electrons show less fragmentation. Interpreted in terms of stability, this does not seem to be in agreement with the calculations shown in fig. 3, as there are no oscillations in the binding-energy curves. It should be appreciated, however, that these calculations pertain to cold clusters, while sputtered clusters are internally hot. Nevertheless, there is an inconsistency between fragmentation data and calculated binding energies for cluster ions.

- Among the larger clusters, Cu_9^+ is a particularly stable one. It is a magic-number cluster, as it contains a 'closed shell' for 8 binding electrons. All clusters composed of more electrons (atoms) show higher decay probabilities.

These results are strongly supported by recent molecular-dynamics calculations of keV Ar→Ag sputtering, using up-to-date metal potentials (Wucher & Garrison, 1992b). There it was found that the majority of the emitted trimers and virtually all the larger clusters fragmented spontaneously in the first nanosecond after emission.

This behaviour could be clearly traced back to the high internal energies with which clusters are 'born'. It is of course to be expected that stable quadrumers and even larger clusters should be detectable in such simulations; computer time restrictions, however, severely impede the simulation of sufficiently many atom impacts to obtain statistical information on large stable clusters.

Thus, fragmentation is a clear sign of the metastable character of sputtered clusters. It must be taken as a warning that measured abundance distributions may only be used with caution to represent the initial, i.e., ejection, cluster distribution. Furthermore, cluster fragmentation underlines the importance of cluster stability for abundance distributions.

3   Energy and Angular Distributions

Kinetic-energy spectra of cluster ions have been measured by many groups. Without exception, they show with increasing cluster size a faster decline of the high-energy tail, cf. fig. 6a.

In the last decade, results for neutral clusters have been obtained as well. The data displayed in fig. 6b have been obtained in an SNMS system using electron ionization, and show similar features as stated for charged clusters above.

In the following, we shall turn to a more detailed description of the characteristics of sputtered dimers. As mentioned in the Introduction, substantial work in this area was performed before the report period, i.e., up to the mid-eighties. We wish to mention in particular the experimental and theoretical work of Snowdon and coworkers as summarized by Snowdon et al. (1986); of Haring, Oostra, de Vries, and others of the FOM-group, which was summarized by de Vries (1987); and of the computer simulation studies of Harrison and coworkers, summarized by Harrison (1983; 1988). Due to these efforts, a considerable body of information on possible mechanisms of the sputtering of dimers and their properties has accumulated. Progress since then is characterized by further detailed experimental information on the one hand, and improved molecular-dynamics simulations on the other, and will now be described.

3.1   Emission of (Preformed) Molecules

Probably the simplest case of cluster sputtering is realized in a solid where (preformed) molecules exist. These are characterized by the condition that the dissociation energy D of the diatomic molecule is large compared to its binding energy U to the surroundings. This case is by definition realized in molecular solids; it may be realized in systems of chemically reactive sputtering, or in the ion-induced
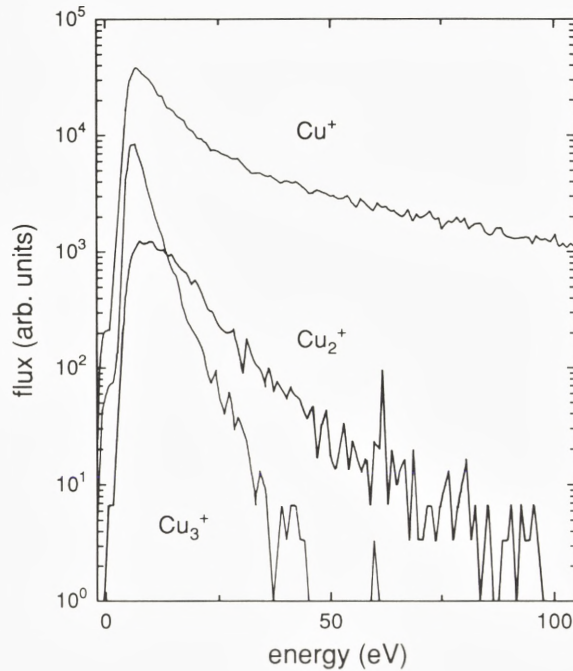
Figure 6a. Kinetic-energy distributions of clusters sputtered from a polycrystalline Cu sample. Ionized clusters Cu_n^+ from 5.5 keV Cs^+ bombardment. Data due to Gnaser (1992)

desorption of molecular adsorbate layers (Taglauer et al., 1980; Sagara & Kamada, 1982).

Measurements on elemental, diatomic molecular solids, such as solid N_2, have only very recently been performed with keV heavy ions (Pedrys, 1993). Under low-energy ion bombardment, a Thompson distribution for the kinetic energy of sputtered N_2-molecules was observed, but with an apparently lowered value of the surface binding energy U as compared to the measured sublimation energy. This may indicate that the surface binding force acts in a more complex manner on dimers, where several more degrees of freedom are active during emission than for atomic particles (Urbassek, 1992).

Otherwise, most measurements have been made on chemically transformed solids, i.e., under conditions of chemically reactive sputtering. Fig. 7 displays the kinetic energy distribution of molecules sputtered under such conditions. The E^{-2}-like decay of the distribution at high energies is strong evidence for the so-called single-collision emission mechanism, in which the molecule emission is induced by
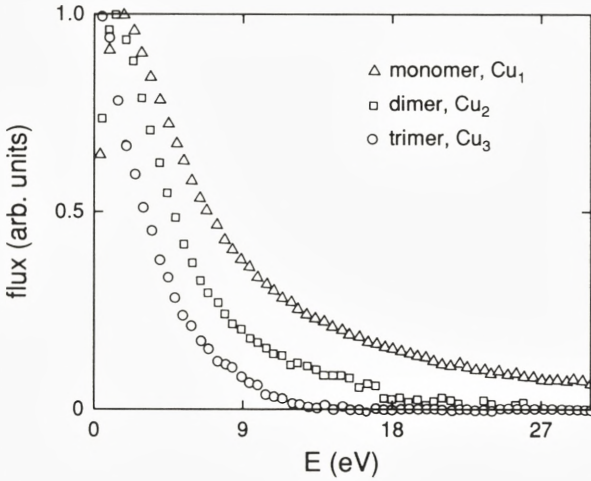
Figure 6b. Same as fig. 6a for neutral clusters Cu_n from 1 keV Ar^+ bombardment. Data taken from Brizzolara & Cooper (1989).

a single collision with a recoil particle of the collision cascade. Under these conditions, the usual argumentation of collision cascade physics applies which predicts an E^{-2} tail of the kinetic energy distribution (Sigmund, 1981). This behaviour has also been found in the emission of monoxide molecules sputtered from oxides or oxygenated surfaces (Wucher & Oechsner, 1987). As above, we note that the nature of the surface binding energy U may be more complex in the case of molecules than in that of atoms.

This so-called single-collision mechanism has been discussed in the literature repeatedly, starting with Benninghoven (1973), and followed by Oechsner et al. (1978), Sigmund et al. (1986), de Jonge et al. (1988), and others. It has been given various names such as 'direct emission', 'intact ejection', 'emission as such', etc. This mechanism allows molecules to receive a high amount of relative kinetic energy E_{rel} without dissociation. This is possible up to $E_{rel} = D$. Since the center-of-mass and the relative energy which the molecule receives in an energetic collision are correlated, dimers with considerable center-of-mass energy can be emitted. Thus, for a homonuclear dimer the E^{-2} distribution will be valid up to a center-of-mass energy of around D. For higher energies, the collision ejecting the molecule will also impart to it such a large amount of internal energy that it breaks up. We note that the emission process at small emission energies $E \lesssim U$ may deviate from this simple picture. At these low energies, the laws underlying collision cascade physics need not necessarily apply any more. Thus, for instance, the molecule moves so
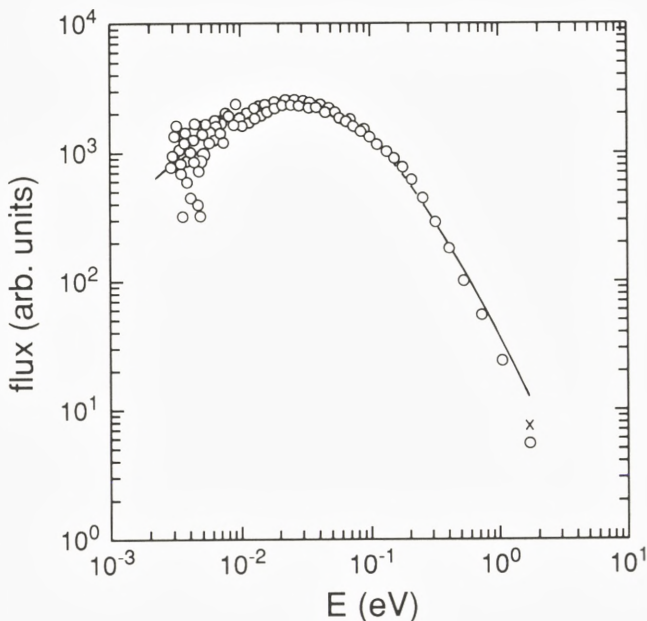
Figure 7. Kinetic-energy distribution of molecules sputtered by 3 keV Ar^+ bombardment from a Si surface in an SF_6 atmosphere at 50 K. The signal is due to both sputtered SiF_3^+ radicals and postionized SiF_4 molecules. Data taken from Oostra et al. (1986).

slowly – the binding energy U is typically below 1 eV – that several recoils may hit it.

The physics underlying the single-collision picture is sufficiently simple that detailed studies of the internal – i.e., rotational and vibrational – degrees of freedom were possible (Snowdon, 1985; Sigmund et al., 1986; de Jonge et al., 1988). A straightforward application of the ideas underlying the single-collision picture gives the following results (Sigmund et al., 1986):

(i) both rotational and vibrational excitation obey an E^{-2} law;

(ii) internal energy is positively correlated with the kinetic energy;

(iii) rotational and vibrational energy are anti-correlated with each other.

De Jonge et al. (1986a; 1986b; 1987), as summarized in de Jonge (1988), performed a detailed experimental study of the internal degrees of freedom of a sputtered dimer for a case where the single-collision mechanism could be assumed to apply. The system chosen was elementary sulphur, which is unfortunately rather a complex system. The S_8-rings, which form elemental sulphur in equilibrium,
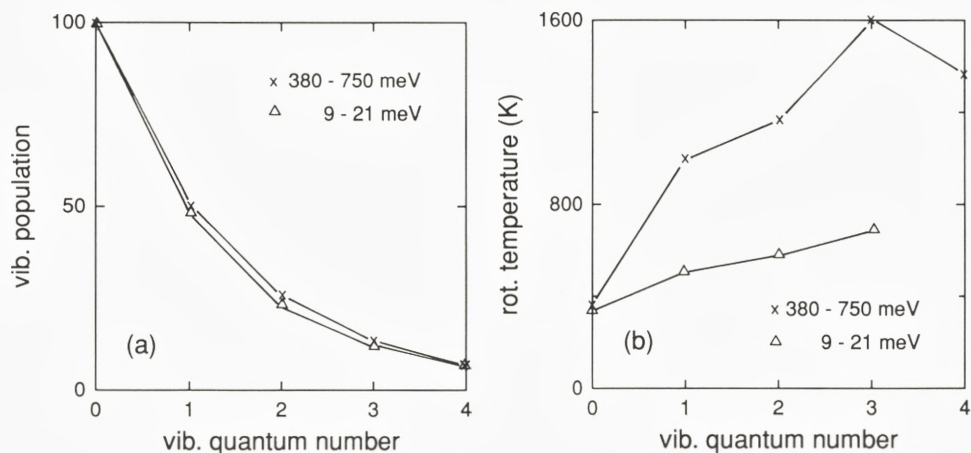
Figure 8. Internal energies of S_2-molecules sputtered by 5 keV Ar^+ ions from sulphur. Measurements are for slow and fast molecules, of kinetic energy $E_{kin} = 9$–21 meV, and 380–750 meV, respectively. a) Population of vibrational levels. b) Mean rotational energy (expressed as a temperature) of molecules sputtered in a specified vibrational level. Data taken from de Jonge et al. (1987).

decompose under ion bombardment; S_2 is the majority species in the sputtered flux (Chrisey et al., 1988). It is assumed that S_2 is also the near-surface majority species in an ion-bombarded sample under steady-state conditions, and that it does not form only during emission or by fragmentation of sputtered S_8-rings. Thus, the single-collision mechanism can be assumed to apply.

Fig. 8 displays the results of such a measurement. It seems that the vibrational distribution decays exponentially rather than like an inverse power – although this is somewhat hard to decide upon the basis of the 5 data points taken. While rotational energy indeed increases with the kinetic energy of the sputtered molecules, vibrational energy appears to be independent of it. And rotation and vibration are positively correlated in contrast to item (iii) above.

These results are in conflict with the simple picture given above. However, at least a qualitative explanation of the measured data was given by de Jonge et al. (1988) and Urbassek (1988a). These authors showed that an improved modeling of the atom-molecule (or molecule-molecule) collision ejecting the molecule is necessary in order to understand the excitation of the internal degrees of freedom of sputtered molecules and their correlation with the kinetic energy.

3.2   Cluster Emission from Elemental Materials

In the majority of elemental materials, such as in metals, the dissociation energy D of a dimer is smaller than the bulk sublimation energy U, or at the most of comparable magnitude. In this case, a single collision which transfers enough center-of-mass energy to a dimer to eject it usually imparts also enough internal energy to destroy it. Thus, unless the surrounding material strongly quenches the internal degrees of freedom, the single-collision mechanism will not work.

Here, a different prototypical mechanism has been proposed (Können et al., 1974; Gerhard, 1975): Consider two atoms ejected in an ion-induced collision cascade from the target. If their momenta are sufficiently aligned and of comparable magnitude, and the trajectories of the two atoms are sufficiently close to each other, the two atoms are bound to each other and form a dimer. Since these conditions impose strong restrictions on the phase space available for dimer formation, a considerably stronger high-energy decay of the kinetic energy E is found than for atomic emission. Calculations[7] show that the distribution decays according to E^{-5} for $E \gg U, D$.

As an extension of the early papers by Können et al. (1974) and Gerhard (1975), theoretical modelling was able to provide more information on emitted dimers. We mention here the angular distribution, the internal – i.e., rotational and vibrational – excitation, and the kinetic-energy distribution at and below the surface binding energy (Snowdon, 1985; Snowdon et al., 1986; Snowdon & Haring, 1987; Haring et al., 1987; Hoogerbrugge & Kistemaker, 1987). However, these quantities depend crucially on the detailed interplay between the intramolecular potential and the surface binding forces. Here, assumptions had to be introduced the validity of which is hard to check by experiment. Realistic molecular-dynamics simulations may improve the modelling.

Experiments show that the kinetic-energy distributions of dimers sputtered from metals are indeed steeper than the E^{-2} decay of the monatomic distribution (Bernhardt et al., 1976; Brizzolara & Cooper, 1989; Coon et al., 1991). However, they approach an E^{-5} law only very slowly, if at all. In the energy window accessible to experiments ($E \lesssim 20U$), the distribution appears to be better characterized by an E^{-3} or E^{-4} decay, as is demonstrated in several papers presented at SPUT92, cf. also fig. 9 below. It is being discussed whether such a behaviour is in agreement with the simple statistical model described above (Urbassek & Gades, 1993).

Molecular-dynamics simulations have for a long time been performed[8] to shed light on cluster emission from metallic targets. Modern simulations use many-body

---

[7]Many of the published calculations contain errors which have their origin in a confusion between phase space density and flux (Haring et al., 1987; Urbassek, 1987).

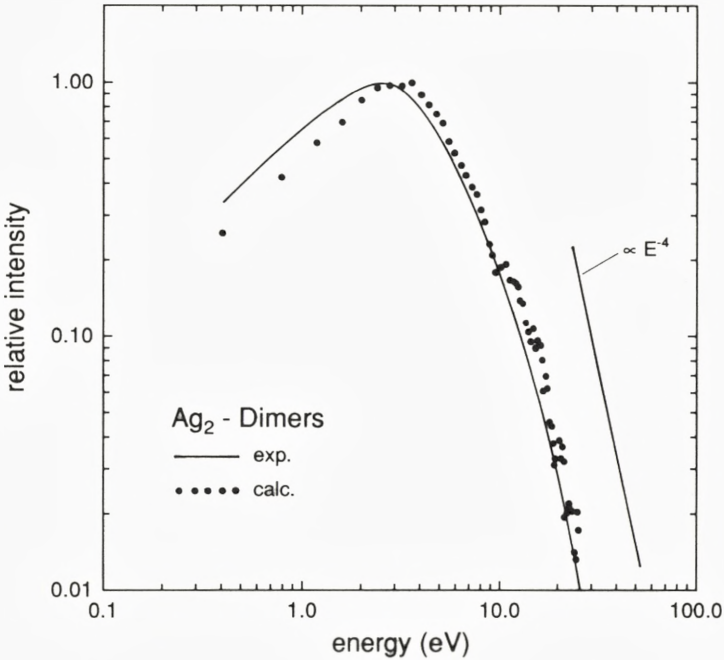[8]For reviews, see Harrison (1983; 1988).

Figure 9. Kinetic-energy distribution of neutral Ag$_2$ dimers sputtered by 1 keV Ar$^+$ ions from polycrystalline Ag. Line: experiment. Dots: simulation. Data taken from Wucher & Garrison (1992a).

potentials, such as the one given by Foiles et al. (1986), and explore the relevant phase space with sufficient statistics to give representative results for dimers emitted from metals. The use of many-body potentials appears important in cluster sputtering studies since the metallic bond cannot be described in terms of pairwise binding potentials, and a proper description of the attractive forces is without doubt of prime importance for the phenomenon of cluster sputtering. In particular, the difference in potential energy, and also in the equilibrium distance, of a dimer before and after ejection can considerably affect the emission characteristics, such as the internal energy, of sputtered clusters. Furthermore, any simulation employing a pair potential derived from bulk properties will underestimate considerably the dimer dissociation energy and hence the sputtered dimer abundance ratio.

Fig. 9 shows molecular-dynamics results for the kinetic-energy distribution of sputtered Ag$_2$ dimers; they are seen to be in good agreement with experiment. The E^{-4} decay indicated in the figure fits the data over some part of the spectrum. However, such simulations allow to extract more data than have been measured up
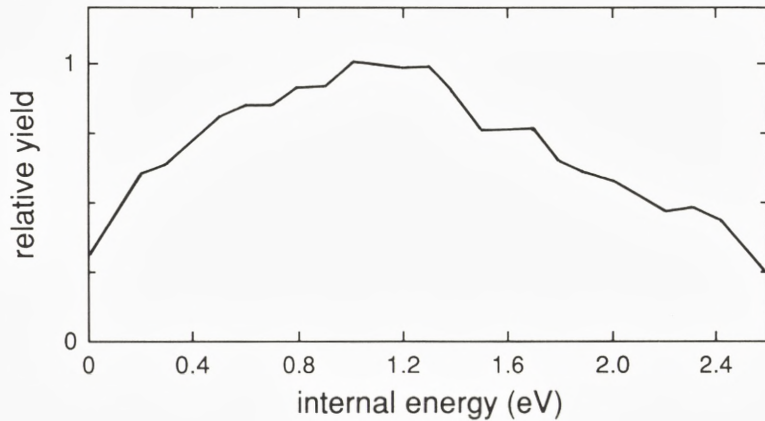
Figure 10. Internal-energy distribution of neutral Ag_2 dimers sputtered by 5 keV Ar^+ ions from Ag (111), as obtained from a molecular-dynamics simulation (Wucher & Garrison, 1992b). Fragmentation products are not taken into account here.

to now. As an example, fig. 10 displays the internal energy distribution of sputtered Ag_2 dimers. It is seen that sputtered clusters are hot, and with only little structure in the distributions. This corroborates the finding of section 2.1 above.

From such simulations it was furthermore found that for keV bombardment of metals, sputtered dimers stem predominantly from nearest-neighbour sites, and that a true double-collision mechanism[9] is responsible for the majority of dimers formed (Karetta & Urbassek, 1992; Betz et al., 1993). The so-called push-and-stick mechanism (Bitensky et al., 1992) is active to a small percentage.

Wucher & Garrison (1992b) demonstrated by molecular-dynamics simulation that fragmentation of large clusters will alter the distribution of dimers which are detected at a macroscopic distance ($\gtrsim 1$ mm) and time ($\gtrsim 1$ μs) after formation: Even though dimers cannot decay in a classical molecular-dynamics simulation in which the electronic degrees of freedom are not taken into account, dimer fragments formed from larger clusters will contribute slow and cool dimers, hence shifting the kinetic-energy distribution to smaller energies, and cooling the internal-energy distribution. Thus, the outcome of a molecular-dynamics simulation stopped several picoseconds after ion impact will not give the same distribution as that measured experimentally.

---

[9]Each of the two atoms, which eventually are to form a dimer, has been knocked on by a different recoil atom.

3.3 Angular Distribution

Cluster emission from polycrystalline surfaces is believed to follow a $\cos^n \vartheta$ distribution, where ϑ is the polar angle of emission, and $n \cong 1 - 2$ (Snowdon & Haring, 1987). Strong deviations from such a smooth distribution must be expected for the desorption of molecules adsorbed on surfaces, and for cluster emission from monocrystalline targets. In the latter case, experiment shows enhanced emission of dimers and trimers along the close-packed lattice directions (Hofer & Gnaser, 1987; Gnaser & Hofer, 1989). We can take this as a natural consequence of momentum alignment. Whatever the reason is for this alignment – focusing collision sequences in the collision cascade or directly induced by the projectile (Karetta & Urbassek, 1992) – any alignment of the recoils' momenta results in a reduction of their relative kinetic energy and, therefore, in an enhanced chance of fulfilling the cluster binding conditions. The striking similarity of the atom and dimer angular distributions observed from single crystals in these experiments appears hard to reconcile with a statistical emission model.

Otherwise, the lattice structure seems to have little effect on cluster emission. The abundance distributions of sputtered Si and Ge clusters at least show no influence of whether the target is in the crystalline or the amorphous state (Gnaser & Hofer, 1989). Abundance distributions in sputtering are, therefore, controlled by the short-range distance-distribution of the atoms in the solid; this is known not to be too dissimilar in crystalline and amorphous solids. As an application of this finding, we note that there is no memory effect of the target's structure in mass distributions. So far, this can be stated only for sputtering in the collision-cascade regime. For the 'softer' erosion techniques, such as sublimation by lasers or electric arcs, influences of the target structure on the mass distribution have been reported.

4 Conclusions

Since the last Symposium on Sputtering in Spitz, Austria, 1986, hardly any area in the field of sputtering has seen an advancement similar to that of cluster emission. This is primarily due to our capability of carrying out controlled measurements with neutral clusters as well as of simulating the ejection process by computers.

Let us first consider those particles which constitute the majority flux of sputtered particles. The emission of atoms, dimers, trimers and quadrumers make up more than 99% of that flux. Conventional methods such as the ionization by electrons and standard mass spectrometry are sufficient for studies of these particles. Larger neutral clusters require the outstanding sensitivity of the laser-ionization technique. It was only recently that this technique was applied to sputtered clusters. Right from the start it has resulted in the identification of clusters as large as

Cu_{15} and Ag_{18}. Although the amount of material emitted in this form is negligible, the ejection process of such agglomerates is interesting in itself.

As far as the phenomenon of sputtering is concerned, several of the long-standing key issues are in the process of being solved now.

- The fraction of bound atoms in the sputtered flux appears to be in the $10-20\%$ range for cascade sputtering. This is low compared to the corresponding number for ionic particles. The reason is, firstly, the steep fall-off in the neutrals' abundance distribution; this is expected to be connected with their reduced binding energy. Secondly, the effect of alternating abundances in the spectra of cluster-ions of monovalent elements is less pronounced or even absent with neutrals; this again reduces the bound-to-monomer emission ratio. It is important to keep in mind, however, that clusters fragment during the first several microseconds after emission. The bound-atom fraction immediately after emission may hence be larger than the measured one. As to sputtering physics, it is clearly the first quantity which is of main interest, since the solid is not involved in the fragmentation process which changes the cluster distribution after emission.

- The energy distribution of sputtered clusters is in the center of interest presently. Several contributions at this conference were concerned with it. Such experiments are plagued with a multitude of instrumental problems and artifacts. The most recent experiments indicate deviations of the measured kinetic-energy distributions from existing analytical theories. Measured distributions appear to be flatter than predicted, and approach those expected for the emission of atoms, or the single-collision ejection of preformed, adsorbed molecules. The origin of these discrepancies is at present unclear.

- Even more complicated is the determination of the distribution of internal energy. Very few experimental data exist for elemental solids. All information available now points towards a high amount of rotational and vibrational energy stored in the cluster. Rather detailed investigations of fragmentation of cluster ions show this energy to be reduced by the 'boiling off' of neutral atoms. This process takes place over a time period of $10\,\mu s$ and more. Great caution is required, therefore, in the interpretation of mass spectra from instruments with different detection time windows with respect to ejection.

We have no information on the fragmentation of neutral clusters. Similar conditions as those with cluster ions are expected. Therefore, here too, measured mass spectra may be far from the ejection distribution. To what extent this holds, depends not only on the clusters' transit time in the spectrometer but also on the energetics of the ionization process. Furthermore, it may be

decisive when after ejection clusters are post-ionized, because the ionization cross section depends on the state of internal energy, and cluster stability depends on both the charge and excitation state.

- The angular distribution of sputtered clusters is largely unknown. For clusters emitted from polycrystalline surfaces, and for not too oblique emission angles, a cosine distribution around the surface normal can be assumed. This need not hold for the emission of preformed molecules.

    Pronounced preferential emission is observed from single-crystal surfaces a-long low-index crystallographic directions. This must be understood as evidence that momentum alignment of recoil atoms or even correlated emission is an important feature in cluster formation.

- Clusters may contain a factor of 3 to 10 more atoms than the average sputtering yield. It is quite generally agreed that this is connected to the statistical variation of the individual cascades. It is unlikely that reaction kinetics based on an average quantity of such poor statistical significance as that of the mean sputtering yield will lead to an understanding of the elementary emission process.

    Computer simulations of the yield per individual cascade show very large fluctuations. These have to be taken into account in any theoretical treatment of cluster sputtering. Simulation by molecular dynamics appears to be predestined to this problem. However, to simulate a sufficient number of atom impacts to put large-cluster emission on a sound statistical basis is a formidable task.

Apart from yielding information on the physics of sputtering, several features of cluster emission upon ion-bombardment of solids are of interest on their own. Strictly speaking, all characteristics typical of cluster-ion emission are of minor relevance to sputtering. However, it was the observation of cluster-ion emission (in SIMS), which has triggered research on sputtering of clusters and which has provided first information on every single quantity discussed in the above chapters. Even in those cases where the information turned out not to be representative of the neutrals, which contribute the majority flux in sputtering, it is still of great importance in the general field of charged-particle emission from solid or liquid surfaces. This is equally true for emission processes of a collisional or a thermal nature, a combination of both – or of quite a different nature such as by electrohydrodynamic forces. As paradigms to such effects may serve the odd-even oscillations in ionized cluster-size distributions of monovalent elements, or the enhanced abundance of magic-number clusters.

We should like to close this review with a word on the two extreme models of cluster emission which have dominated the debate for a long time, i.e., emission as such vs. the association of independently emitted recoils in the transition region between the surface and vacuum. Most workers in this field will agree that these two models should not be interpreted in an extreme sense. Neither does association of independently energized atoms mean that they recombine in vacuum, nor does ejection as such mean that the atoms of the cluster have the same neighboring geometry as they had while they were in the solid; ejection as such is not meant as an ejection of preformed particles. If a rearrangement of atoms in the cluster-to-be is allowed during its passage through the surface, the two models mean the same thing. What is excluded, is a combination of atoms which had not remained in their mutual attraction field before they left the solid.

Acknowledgements

References

Abdullaeva MK, Atabaev BG and Dzabbarganov R, 1991: Nucl. Instr. Meth. **B62**, 43

Andersen HH, 1989: Vacuum **39**, 1095

Baranov IA, Novikov AC, Obnorskii VV, Tsepelevich SO, Kozlov BN and Pilyugin II, 1992: Nucl. Instr. Meth. **B65**, 177

Begemann W, Meiwes-Broer KH and Lutz HO, 1986: Phys. Rev. Lett. **56**, 2248

Begemann W, Dreihöfer S, Meiwes-Broer KH and Lutz HO, 1986: Z. Phys. **D3**, 183

Begemann W, Dreihöfer S, Meiwes-Broer KH and Lutz HO, 1987: In *The Physics and Chemistry of Small Clusters*, edited by P Jena (Plenum, New York), p. 269

Behrisch R, ed., 1981: *Sputtering by particle bombardment I* (Springer, Berlin)

Behrisch R, ed., 1983: *Sputtering by particle bombardment II* (Springer, Berlin)

Behrisch R and Wittmaack K, eds., 1991: *Sputtering by particle bombardment III* (Springer, Berlin)

Benninghoven A, 1973: Surf. Sci. **35**, 427

Bernhardt F, Oechsner H and Stumpe E, 1976: Nucl. Instr. Meth. **132**, 329

Betz G, Husinsky W, Varga P and Viehböck F, eds., 1987: *Symposium on Sputtering* Nucl. Instr. Meth., Vol. 18, p. 321 ff

Betz G, Kirchner R, Husinsky W, Urbassek HM and Rüdenauer F, 1993: Radiat. Eff. Def. Sol. **25**, in press.

Bhaskar ND, Frueholz RP, Klimcak CM and Cook RA, 1987: Phys. Rev. **B36**, 4418

Bitensky IS, Parilis ES and Wojciechowski IA, 1992: Nucl. Instr. Meth. **B67**, 595

Blaise G and Slodzian G, 1968: C. R. Acad. Sci. B **266**, 1525

Bonacic-Koutecky V, Cespiva L, Fantucci P and Koutecky J, 1993a: Z. Phys. D **26**, 287

Bonacic-Koutecky V, Cespiva L, Fantucci P and Koutecky J, 1993b: J. Chem. Phys. **98**, 7981

Brizzolara RA and Cooper CB, 1989: Nucl. Instr. Meth. **B43**, 136

Campana JE, Barlak TM, Colton RJ, DeCorpo JJ, Wyatt JR and Dunlap BI, 1981: Phys. Rev. Lett. **47**, 1046

Chrisey DB, Boring JW, Johnson RE and Phipps JA, 1988: Surf. Sci. **195**, 594

Conrad U and Urbassek HM, 1990: Nucl. Instr. Meth. **B48**, 399

Coon SR, Calaway WF, Burnett JW, Pellin MJ, Gruen DM, Spiegel DR and White JM, 1991: Surf. Sci. **259**, 275

Cooper CB and Hamed HA, 1984: Surf. Sci. **143**, 215

de Jonge R, 1988: Comments At. Mol. Phys. **22**, 1

de Jonge R, Baller T, Tenner MG, de Vries AE and Snowdon KJ, 1986a: Nucl. Instr. Meth. **B17**, 213

de Jonge R, Baller T, Tenner MG, de Vries AE and Snowdon KJ, 1986b: Europhys. Lett. **2**, 449

de Jonge R, Benoist KW, Majoor JWF, de Vries AE and Snowdon KJ, 1987: Nucl. Instr. Meth. **B28**, 214

de Jonge R, Los J and de Vries AE, 1988: Nucl. Instr. Meth. **B30**, 159

de Vries AE, 1987: Nucl. Instr. Meth. **B27**, 173

Dennis E and MacDonald RJ, 1972: Radiat. Eff. **13**, 243

Dörnenburg E, Hintenberger H and Franzen J, 1961: Z. Naturforschg. **16a**, 532

Downey SW, Emerson AB and Kopf RF, 1992: Nucl. Instr. Meth. **B62**, 456

Dunlap BI, 1982: Surf. Sci. **121**, 260

Dunlap BI, Campana JE, Green BN and Bateman RH, 1983: J. Vac. Sci. Technol. **A1**, 432

Dzhemilev NK and Verkhoturov SV, 1985: Izv. Akad. Nauk SSSR, Ser. Fiz. **49**, 1831 (Bull. Acad. Sci. USSR, Phys. Ser. **49**, 160)

Dzhemilev NK, Rasulev UK and Verkhoturov SV, 1987: Nucl. Instr. Meth. **B29**, 531

Dzhemilev NK, Verkhoturov SV and Veriovkin IV, 1990: Nucl. Instr. Meth. **51**, 219

Dzhemilev NKH, Goldenberg AM, Veriovkin IV and Verkhoturov SV, 1991: Int. J. Mass Spectr. Ion Proc. **107**, R19

Eckstein W, 1988: Nucl. Instr. Meth. **33**, 489

Ens W, Beavis R and Standing KG, 1983: Phys. Rev. Lett. **50**, 27

Fayet P, Wolf JP and Wöste L, 1986: Phys. Rev. **B33**, 6792

Foiles SM, Baskes MI and Daw MS, 1986: Phys. Rev. **B33**, 7983

Franzreb K, Wucher A and Oechsner H, 1991a: Phys. Rev. **B43**, 14396

Franzreb K, Wucher A and Oechsner H, 1991b: Fresenius J. Anal. Chem. **341**, 7

Fürstenau N and Hillenkamp F, 1981: Int. J. Mass Spectr. Ion Phys. **37**, 135

Gerhard W, 1975: Z. Phys. **B22**, 31

Gerhard W and Oechsner H, 1975: Z. Phys. **B22**, 41

Gnaser H, 1992: Private communication

Gnaser H and Hofer WO, 1989: Appl. Phys. **A48**, 261

Gnaser H and Oechsner H, 1991: Nucl. Instr. Meth. **B58**, 438

Gnaser H and Oechsner H, 1993: Nucl. Instr. Meth. **B 82**, 347

Hahn O, Straßmann F, Mattauch J and Ewald H, 1942: Naturwissenschaften **30**, 541

Haring RA, Roosendaal HE and Zalm PC, 1987: Nucl. Instr. Meth. **B28**, 205

Harrison Jr. DE, 1983: Radiat. Eff. **70**, 1

Harrison Jr. DE, 1988: Crit. Rev. Solid State Mater. Sci. **14**, S1

Harrison Jr. DE and Delaplain CB, 1976: J. Appl. Phys. **47**, 2252

Herzog RFK, Poschenrieder WP and Satkiewicz FG, 1973: In *Ion Surface Interaction, Sputtering and Related Phenomena*, edited by R Behrisch, W Heiland, W Poschenrieder, P Staib and H Verbeek (Gordon and Breach, London), p. 173; also published as: Radiat. Eff. **18**, 199

Hofer WO, 1980: Nucl. Instr. Meth. **170**, 275

Hofer WO, 1986: In *Erosion and Growth of Solids Stimulated by Atom and Ion Beams*, edited by G Kiriakidis, G Carter and JL Whitton (Nijhoff, Dordrecht), p. 1

Hofer WO, 1991: In *Sputtering by particle bombardment III*, edited by R Behrisch and K Wittmaack (Springer, Berlin), p. 15

Hofer WO and Gnaser H, 1987: Nucl. Instr. Meth. **B18**, 605

Honig RE, 1953: J. Chem. Phys. **21**, 573

Honig RE, 1954: J. Chem. Phys. **22**, 126

Honig RE, 1958: J. Appl. Phys. **29**, 549

Hoogerbrugge R and Kistemaker PG, 1987: Nucl. Instr. Meth. **B21**, 37

Hortig G and Müller M, 1969: Z. Phys. **221**, 119

Jackschath C, Rabin I and Schulze W, 1992: Z. Phys. **D22**, 517

Jonkman HT and Michl J, 1981: J. Am. Chem. Soc. **103**, 733

Joyes P, 1971: J. Phys. **B4**, L15

Joyes P, van der Walle J and Colliex C, 1986: Ultramicroscopy **20**, 65

Joyes P and Sudraud P, 1985: Surf. Sci. **156**, 451

Karetta F and Urbassek HM, 1992: Appl. Phys. **A55**, 364

Katakuse I, Ichihara T, Fujita Y, Matsuo T, Sakurai T and Matsuda H, 1985: Int. J. Mass Spectr. Ion Proc. **67**, 229

Kelly R, 1984: Radiat. Eff. **80**, 273

Klimovskii YA, 1987: Zh. Tekh. Fiz. **57**, 1951 (Sov. Phys. Tech. Phys. **32**, 1173)

Klots CE, 1985: J. Chem. Phys. **83**, 5854

Klots CE, 1991: Z. Phys. **D21**, 335

Können GP, Tip A and de Vries AE, 1974: Radiat. Eff. **21**, 269

Krohn Jr. VE, 1962: J. Appl. Phys. **33**, 3523

Leleyter M and Joyes P, 1973: In *Ion Surface Interaction, Sputtering and Related Phenomena*, edited by R Behrisch, W Heiland, W Poschenrieder, P Staib and H Verbeek (Gordon and Breach, London), p. 185; also published as: Radiat. Eff. **18**, 105

Magnera TF, David DE and Michl J, 1985: Chem. Phys. Lett. **83**, 2594

Makarenko BN, Popov AB, Shaporenko AA and Shergin AP, 1991: Radiat. Eff. Defects Solids **116**, 15

Mattauch J, Ewald H, Hahn O and Straßmann F, 1943: Z. Phys. **120**, 598

Merkle KL and Jäger W, 1981: Philos. Mag. **A44**, 741

Oechsner H, 1985: In *Symposium on Physics of Ionized Gases, SPIG 1984*, edited by MM Popovic and P Krstic (World Scientific, Singapore), p. 571

Oechsner H, 1990: Int. J. Mass Spectr. Ion Proc. **103**, 31

Oechsner H, Schoof H and Stumpe E, 1978: Surf. Sci. **76**, 343

Oostra DJ and de Vries AE, 1987: Nucl. Instr. Meth. **B18**, 618

Oostra DJ, Haring A, de Vries AE, Sanders FHM and van Veen GNA, 1986: Nucl. Instr. Meth. **B13**, 556

Orth RG, Jonkman HT, Powell DH and Michl J, 1981: J. Am. Chem. Soc. **103**, 6026

Pedrys R, 1993: Oral contribution at *SPUT92*

Powers DE, Hansen SG, Geusic ME, Michalopoulos DL and Smalley RE, 1983: J. Chem. Phys. **78**, 2866

Reimann CT, 1993: Mat. Fys. Medd. Dan. Vid. Selsk. **43**, 351

Rodriguez-Murcia H and Beske HE, 1978: Adv. Mass Spectrom. **7**, 598

Sagara A and Kamada K, 1982: J. Nucl. Mater. **111&112**, 812

Schou J and Hofer WO, 1982: Appl. Surf. Sci. **10**, 383

Sigmund P, 1977: In *Inelastic ion-surface collisions*, edited by NH Tolk, JC Tully, W Heiland and CW White (Academic Press, New York), p. 121

Sigmund P, 1981: In *Sputtering by particle bombardment I*, edited by R Behrisch (Springer, Berlin), p. 9

Sigmund P, 1987: Nucl. Instr. Meth. **B27**, 1

Sigmund P, 1993: Private communication

Sigmund P, Urbassek HM and Matragrano D, 1986: Nucl. Instr. Meth. **B14**, 495

Snowdon K, 1985: Nucl. Instr. Meth. **B9**, 132

Snowdon KJ and Haring RA, 1987: Nucl. Instr. Meth. **B18**, 596

Snowdon KJ and Heiland W, 1984: Z. Phys. **A318**, 275

Snowdon KJ, Willerding B and Heiland W, 1986: Nucl. Instr. Meth. **B14**, 467

Staudenmaier G, 1972: Radiat. Eff. **13**, 87

Staudenmaier G, 1973: In *Ion Surface Interaction, Sputtering and Related Phenomena*, edited by R Behrisch, W Heiland, W Poschenrieder, P Staib and H Verbeek (Gordon and Breach, London), p. 181; also published as: Radiat. Eff. **18**, 181

Taglauer E, Heiland W and Onsgaard J, 1980: Nucl. Instr. Meth. **168**, 571

Thomas EW and Efstathiou L, 1984: Nucl. Instr. Meth. **B2**, 479

Thum F and Hofer WO, 1979: Surf. Sci. **90**, 331

Urbassek HM, 1987: Nucl. Instr. Meth. **B18**, 587

Urbassek HM, 1988a. Habilitationsschrift, TU Braunschweig, Germany

Urbassek HM, 1988b: Nucl. Instr. Meth. **B31**, 541

Urbassek HM, 1989: Radiat. Eff. Defects Solids **109**, 293

Urbassek HM, 1992: J. Phys.: Condens. Matter **4**, 4871

Urbassek HM and Gades H, 1993: In preparation

Wada M, Tsuda H and Sasao M, 1991: Jap. J. Appl. Phys. **30**, L2133

Winograd N, Harrison Jr. DE and Garrison BJ, 1978: Surf. Sci. **78**, 467

Winograd N, Foley KE, Garrison BJ and Harrison Jr. DE, 1979: Phys. Lett. **73A**, 253

Wittmaack K, 1979: Phys. Lett. **69A**, 322

Woodyard JR and Cooper CB, 1964: J. Appl. Phys. **35**, 1107

Wucher A, 1993: Private communication

Wucher A and Garrison BJ, 1992a: Surf. Sci. **260**, 257

Wucher A and Garrison BJ, 1992b: Phys. Rev. **B46**, 4855

Wucher A and Oechsner H, 1987: Nucl. Instr. Meth. **B18**, 458

Wucher A, Wahl M and Oechsner H, 1993: Nucl. Instr. Meth. **B 82**, 337

Wurz P, Husinsky W and Betz G, 1991: Appl. Phys. **A52**, 213

Yu ML, 1981: Phys. Rev. **B24**, 1147; 5625

Yu ML, 1982: Appl. Surf. Sci. **11/12**, 196

Yu ML, 1991: In *Sputtering by particle bombardment III*, edited by R Behrisch and K Wittmaack (Springer, Berlin), p. 91