Nonlinear Effects in Collisional Sputtering under Cluster Impact

By Hans Henrik Andersen
The Niels Bohr Institute, Ørsted Laboratory,
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Synopsis

Experimental evidence for peculiar sputtering effects under cluster impact of metals is discussed. It is emphasized that these effects, seen mainly as excessive yields, are also found for heavy single-atom impacts on heavy target materials and are connected with high energy-deposition densities in the surface region. The data are discussed in relation to a number of explanations put forward and found to be compatible only with spike effects and to somė extent with lowering of surface energies due to emission of clusters. Recent computer simulations of cluster impacts will also be discussed. A number of cases where experimental data are badly missed will be pointed out and some experiments suggested.

1 Introduction

When a solid target is sputtered with a molecule or a cluster of atoms the sputtering yield may deviate from the sum of the yields of the individual atoms at the cluster velocity (Andersen & Bay, 1974). Such experimental nonlinear effects which in practice nearly always manifest themselves as enhanced yields, are the topic of the present review. An extensive review of such effects has not been given since that of Thompson (1981a; see also 1980). He discussed the phenomenon in the broad context of sputtering, radiation damage, gas desorption and ion beam mixing and suggested a number of explanations for the observed phenomena. Few systematic experimental investigations have been presented since 1981, but a number of scattered data and ideas relevant for the subject have appeared. I shall here discuss only the collisional sputtering aspects of cluster impact but shall try to cover the experimental side of this topic completely to allow a discussion of the problems raised by Thompson in his 1981 review. Nonlinear phenomena are also seen in electronic sputtering but these effects will not be discussed here. For a general discussion of electronic sputtering see Townsend (1983) and for a discussion of some of the electronic nonlinear effects see Johnson & Schou (1993).

Nonlinear effects may also be defined from a theoretical viewpoint. The analytical theory of collisional sputtering (Sigmund 1969, 1981) is established through solving of a Boltzmann transport equation describing the collision cascade. As an essential step in obtaining a solution of this equation, it has been linearized. Physically this means that moving atoms within the collision cascade are supposed to collide only with resting atoms, i.e., a moving atom will always loose and never gain energy through a collision. The solution of the linearized equation shows that the energy spectrum of the atoms set in motion within the cascade is approximately proportional to the inverse square of their starting energy. Hence at sufficiently low recoil energy any atom within the cascade volume has been set in motion and the linearity assumption breaks down. If this breakdown occurs at an energy that is very low compared to energies characteristic for the sputtering process, e.g. the sublimation energy, no consequences are expected for the sputtering yield. The higher the energy density within the cascade, the higher the breakdown energy. A way to enhance the energy density is through cluster bombardment. Hence nonlinear experimental effects may be directly related to the behaviour caused by the breakdown of the linearized Boltzmann equation.

The main theoretical result for the sputtering yield is

$$Y = 0.042\ \alpha(M_2/M_1)\frac{S_{\mathrm{n}}(E, Z_1, Z_2)}{U_{\mathrm{s}}\text{Å}^2}, \tag{1}$$

where α is a numerically calculated function of the target-to-projectile atom mass ratio M_2/M_1. S_{n} is the nuclear stopping cross section, which is a function of the projectile and target atomic numbers Z_1 and Z_2 and the projectile energy E. Note that this energy enters essentially through S_{e}. Finally, U_{s} is the surface binding energy, for metals mostly taken to be the sublimation energy.

Eq. (1) is usually considered to give a good fit to experimental sputtering yields if the projectile energy is above a few keV and if the energy density deposited at the target surface is not too high. There may, however, be several reasons for deviations from eq. (1), most of them non-related to the present review. Andersen & Bay (1981) discussed the region of applicability in connection with their yield-data graphs. For a number of elements, where the absolute yields are not well represented by eq. (1), the projectile-energy dependence is nevertheless given by S_{n}, except for large S_{n} in heavy targets, i.e. where the deposited-energy density is high.

When the energy spectrum of recoil atoms is modified by slowing down and by escape from the solid, the spectrum of sputtered atoms is found to be

$$\frac{dY}{dE_1} \simeq \frac{cE_1}{(E_1 + U_3)^3}, \tag{2}$$

the Thompson spectrum (Thompson, 1968). Also from this formula we expect minor deviations non-related to our present topic (Sigmund 1981, 1987), but it is clear from the discussion above that if the yield is influenced by nonlinear effects, such effects must also appear as a significant deviation from eq. (2) for small E_1.

It is not intuitively clear whether nonlinear effects will cause the yield to decrease or to be enhanced. On the one hand, within the nonlinear cascade fewer atoms are set in motion than within the linear cascade. On the other hand the moving atoms cannot get rid ot their energy. Hence the cascade will live longer. As already mentioned above, we usually find an increase. We must expect these 'extra' sputtered atoms to be of low energy, thus adding a low-energy component to the spectrum.

The connection between experimental and theoretical nonlinear effects was mentioned above. Note that we observe nonlinearities experimentally. Thompson (1981b) on the other hand argued against the use of the term nonlinear effects. It appears that this argumentation is based on the misconception that nonlinear effects should also imply that collisions may not be treated as binary (see also Johar & Thompson, 1979 for a similar statement). I maintain that linear as well as nonlinear cascade theory may be based on binary collisions, and shall hence continue to use the term 'nonlinear'.

The spatial region where a very dense collisional cascade is propagating is usually called a spike. A number of different adjectives like 'thermal', 'collisional', 'displacement', etc. have been connected with the spike. I shall only use the pure word as such. Sputtering from spikes has of course also been modelled. Sigmund (1974), Sigmund & Claussen (1981) and Johnson (1987) presented theories for sputtering from such spikes, while Sigmund & Szymonski (1984) also discussed what happens after the collisional part of the spike has passed (t $> 10^{-11}$ sec). Collective mechanisms like gas flow (David et al., 1986; Urbassek & Michl, 1987) and shock waves (Carter, 1979; Kitazoe & Yamamura, 1980; Bitensky & Parilis, 1987) have also been treated. Common to most theoretical treatments is the concept of a spike lifetime considerable longer than that of the linear cascade (Sigmund, 1974, 1975, 1977). Some aspects of these theories are discussed by Johnson & Schou (1993), but as only very few experimental data allow anything like a detailed quantitative comparison, I shall not discuss which spike theories may be most relevant. Experimental data do, on the other hand, allow to rule out a number of non-spike theories as discussed below.

Before presenting experimental data, we need eventually to discuss some nomenclature for clusters. Usually a distinction is made between clusters and molecules: Clusters are homatomic, molecules heteroatomic. But this is not consistent with chemical usage: We talk about the O_2 or O_3 molecule. Sizewise, Harrison & Edwards (1985) proposed a hierarchy of names. With 2-10 atoms they speak about clusters, for 10-100 atoms of aggregates, for 100 to 10000 atoms of ultrafine particles and for larger sizes simply of particles. Kofman et al. (1990) remark that this classification is not fully established. This is certainly true within the ion-beam communities. Here the terms atoms, dimers and trimers are used for conglomerates of two and three identical atoms but anything containing from 2 to 10000 atoms may be called a cluster. For even larger sizes, we talk about particles. This nomenclature is essentially in agreement with the one advocated by Beuhler & Friedman (1986) and Mathew et al. (1986). Finally, it is worth mentioning that Hayashi (1987) calls attention to the fact that the term aggregate ought to be reserved for irregularly shaped objects.

2 The Experimental Data

In this section a number of experimental data relevant for the elucidation of cluster-impact effects on sputtering will be presented. The data, the method by which they are obtained, and the motivation for treating them in this section will be discussed. Whether the data allow to discern between different theories of nonlinear effects will, in contrast, first be treated in the general discussion section below.

As mentioned in the introduction, nonlinear effects on sputtering yields were postulated to occur before dimer irradiations were performed. Sigmund (1969) showed comparisons between sputtering data and theoretical predictions. While experimental yields from Ar irradiation of Cu, Ag, and Au followed the theoretical predictions rather well, yields from Kr irradiations of Ag of Au showed a moderate enhancement around the yield maximum (via eq. (1) expected to occur at the same energy as the maximum in S_n), while yields from Xe bombardment showed a moderate enhancement in copper and a strong one ($\sim$ factor 2) in Ag and Au. Due to the difficulties of the Sigmund (1969) theory to reproduce the yields of low-yield materials, similar comparisons are difficult to make for those, and fewer data exist. It seems, however, that such enhancements of yields under atomic bombardment are not found for low-yield (high surface-binding-energy) materials (Andersen & Bay, 1981; Thompson, 1980). Enhancements are seen for high-yield materials if the stopping power is high (high Z_1; close to maximum in S_n) and the recoil ranges are short (high Z_2) as seen in fig. 1. Hence, enhanced yields are seen for high energy deposition in the surface region. (See also Sigmund, 1987).

The above statement is strongly corroborated by the systematic relative-yield

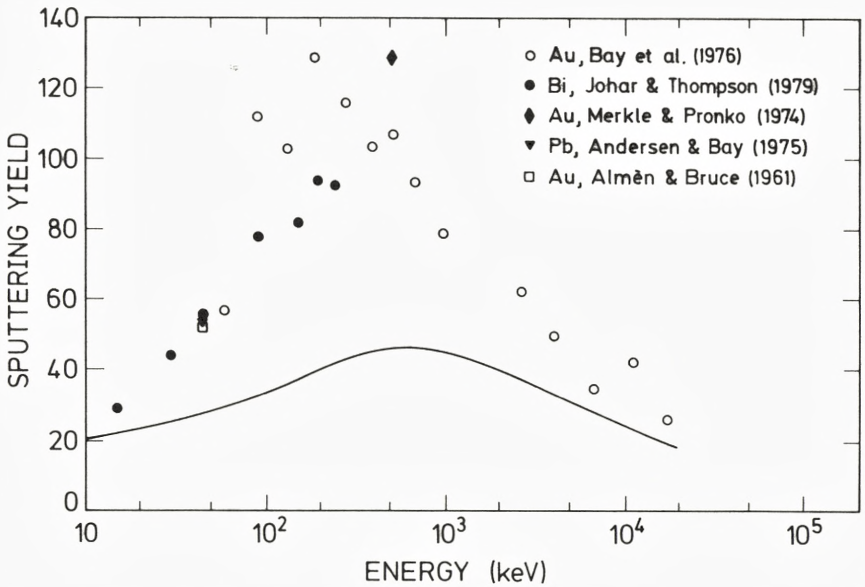

Figure 1. Gold sputtering yields under bismuth, lead, and gold bombardment. The full line represents eq. (1).

measurements performed by Andersen & Bay (1972, 1973, 1975). Their data are presented in fig. 2. Again it is seen that while the Sigmund theory predicts the Z_1 dependence of the yield at 45 keV well for silicon and nicely for copper, strong enhancements of heavy-ion yields relative to Ar sputtering are seen for silver and gold. The enhancements comprise in both cases a factor of 2.5 for the heavy projectiles.

Based on the reviews by Thompson (1980, 1981a), Zalm & Beckers (1984) conjectured that nonlinear effects should show up whenever Y exceeded 7[1]. Therefore they measured yields of zinc (U_s = 1,35 eV) bombarded by low-energy (0.2 - 20 keV) Xe atoms. The yields covered the region from 3 to 28 and closely follow the energy dependence of the nuclear stopping power, which is surprising as the energy extends well below the point where collision-cascade theories are expected to apply. The data fit nicely together with the 45 keV point obtained by Almen & Bruce (1961). That the $Y = 7$ limit does not apply for lighter targets may also be seen from the Kr yield of copper (Andersen & Bay, 1981; fig. 4.16). The energy

[1]On the other hand, Sigmund & Claussen (1981) stated $Y_{rmlinear} > 10$ as a necessary condition for significant nonlinear sputtering. This is in good agreement with the experimental data of Oliva-Florio et al. (1979, 1987)

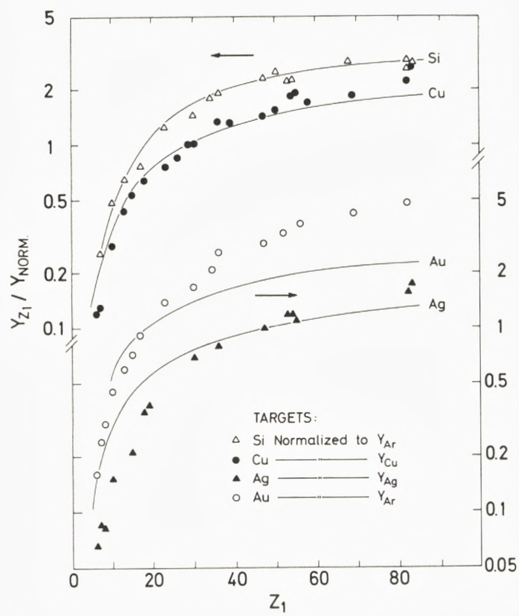

Figure 2. Relative Si, Cu, Ag, and Au sputtering yields for 22 different ions at 45 keV. Data from Andersen & Bay (1972, 1973 and 1975).

dependence follows that of S_n strictly from 2 to 1000 keV, while the yield rises to 14. Obviously the condition of short recoil ranges has not been taken into account in the argumentation of Zalm & Beckers. Notwithstanding, yield measurements for a very-high yield material like Zn would be most interesting for higher Xe energies. Such measurements are difficult as Zn is no easy target material to work with. Zalm and Beckers demonstrate by their careful measurements how such a task may be accomplished experimentally.

Nonlinear effects may be seen for light elements at low energies provided the binding energy is low enough. This is the case for condensed rare gases. The energies must be kept low to ensure collisional sputtering as these targets are otherwise sputtered heavily electronically. Fig. 3 shows data for 1-5 keV Ar, Kr and Xe sputtering of neon by Balaji et al. (1989). The yields rise much faster than proportional to S_n (an apparent slope of 1 would correspond to $Y \propto (S_n)^6$. In this case the surface binding energy is extremely low (40 meV). Balaji et al. also performed measurements on argon, krypton and xenon, where the increase of the

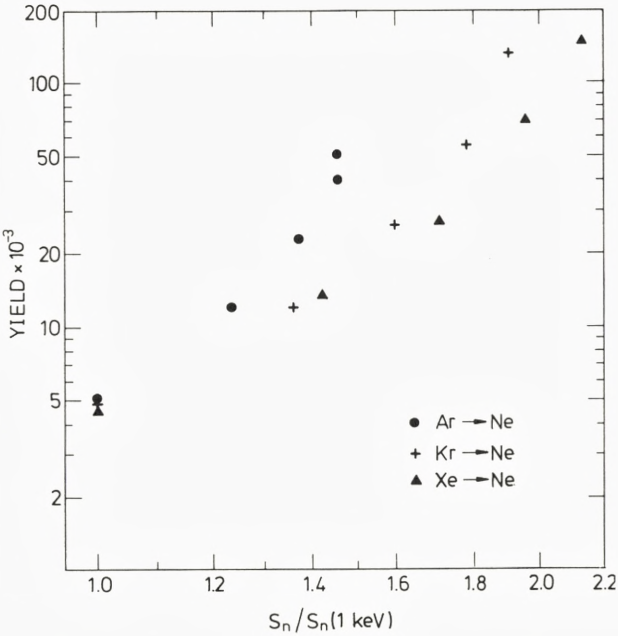

Figure 3. Sputtering yields for condensed neon bombarded by 1 - 5 keV rare gas ions as a function of the relative nuclear stopping $S_n(E)/S_n(1\text{keV})$. The horizontal scale has been stretched by a factor of 6. A slope of 1 would hence correspond to $Y \propto (S_n)^6$. Yield data are from Balaji et al. (1990).

yield with S_n is somewhat slower. Further data at slightly higher energies are given by Schou et al. (1992), and a more detailed discussion of the argon yields is given by Johnson & Schou (1993).

The evidence discussed above and mostly known prior to 1974 prompted Andersen & Bay (1974) to attempt a direct experimental proof of the existence of nonlinear effects. Silicon, silver and gold were bombarded with the dimers Cl_2, Se_2 and Te_2 and the corresponding monomers at the same energy per atom. While no significant enhancement was found for Cl_2 irradiation, Se_2 yielded in all cases an enhancement, the larger the heavier the target. An example is shown in Fig. 4. It is important that the measurements be performed alternately with monomers and dimers. In this way neither chemical effects nor topographic changes of the surface will influence the measured enhancement factors.

A few cluster bombardments were reported earlier. Grønlund & Moore (1960) bombarded silver with H and H_2 at low energies. In hindsight it is not surprising that they saw no enhancement with such light projectiles. In contrast, Rol et al.

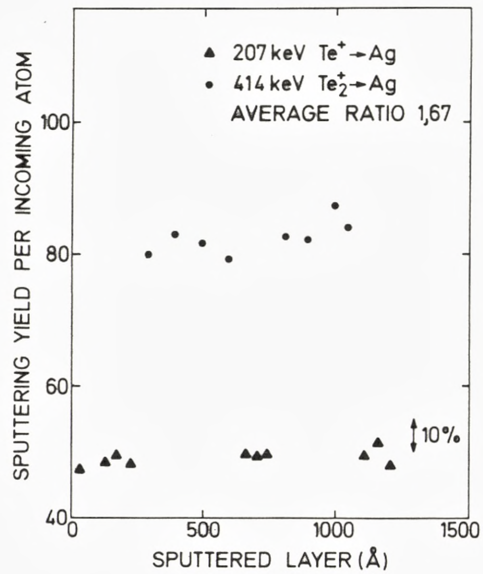

Figure 4. Sputtering yield per atom of a polycrystalline silver target for 207 keV Te^+ and 414 keV Te_2^+ ion bombardment as a function of sputtered-layer thickness. (From Andersen & Bay, 1974).

(1960) irradiated copper with 5-25 keV KJ^+ and found a 15% enhancement over the sum of the atomic yields. For N_2 irradiations they saw no particular effects. They were mildly puzzled by the KJ^+ results. It is not clear whether chemical effects could have influenced their results, but they appear reasonable in view of later data. Andersen & Bay (1975) also measured the enhancement factor for Te_2 and Se_2 on gold as a function of energy. The enhancement factors stay approximately constant over a factor of ten in energy from the stopping maximum and downwards. Above the stopping maximum, the enhancement factors decrease rapidly with increasing energy.

The energy dependence at low energy was studied by Oliva-Florio et al. (1979). They used 1-50 keV Xe and Xe_2 on Au. Their results are reproduced here as Fig. 5. The energy dependence appears to fit nicely to other experiments. The nonlinear effects are seen to persist down to a reduced energy $\varepsilon = 0.0015$ ($E = 2$ keV). Maybe there is even a cross-over giving rise to the enhancement factors being below 1.0 at lower energies. As mentioned in the discussion section, such a result would not be unreasonable. The measurements were later followed up (Oliva-Florio et al., 1987) with Ar_2 measurements on Au and Xe_2 measurements on Cu, all in the energy

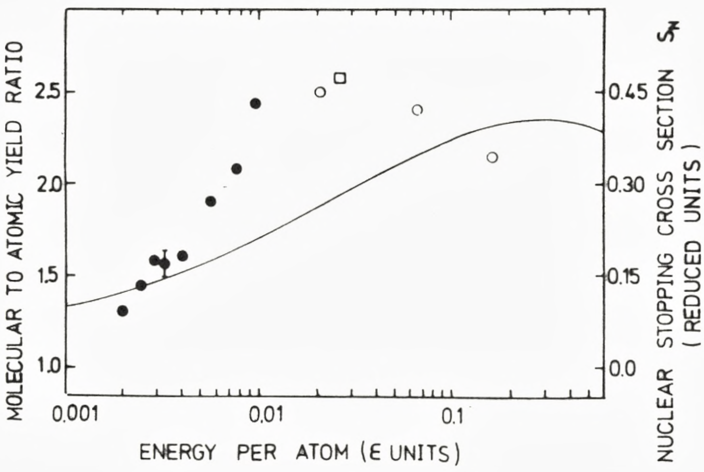

Figure 5. Nuclear stopping powers (full curve) and yield-enhancement factors for molecular irradiations of gold. Filled circles Xe_2 (Oliva-Florio et al., 1979). Open circles Te_2 (Andersen & Bay, 1974), square Sb_2 (Thompson & Johar, 1979) From Oliva-Florio et al. (1979).

interval described above. Ar_2 on Au showed a weak nonlinear effect (enhancement factor ~ 1.2) while the Xe_2 on Cu showed an enhancement factor nearly as large as on Au. With the Cu result perhaps on the high side, the results fit nicely into the trend of other measurements discussed in this section.

Johar & Thompson (1979) and Thompson & Johar (1979 and 1981) carried out a large systematic series of measurements of cluster effects. They bombarded Ag, Au and Pt with P, As, Sb and Bi monomers, dimers, and, for Sb, trimers over the energy range 10-250 keV. For Sb_3 enhancement factors as large as 10 were found. Further, in the 1981 paper they published results on the influence of the bombarding angle. The enhancement factors decreased slightly for incidence angles far away from the target normal, but due to the variation of the yield with incidence angle, yields close to 2000 were reached. The yields are depicted in Fig. 6 as a function of surface-deposited energy. Note that F_D is calculated through a Monte-Carlo procedure. This may be most reasonable for large incidence angles, but published calculations for gold at perpendicular incidence (Thompson, 1981b) show agreement with analytical values at 100 keV yet nearly a factor-of-two below at 1000 keV. All qualitative arguments indicate that the influence of the surface (the main reason for discrepancies between analytical and MC calculations) should decrease with increasing projectile energies rather than the opposite. Hence some doubt remains with respect to the MC calculations. The data from the

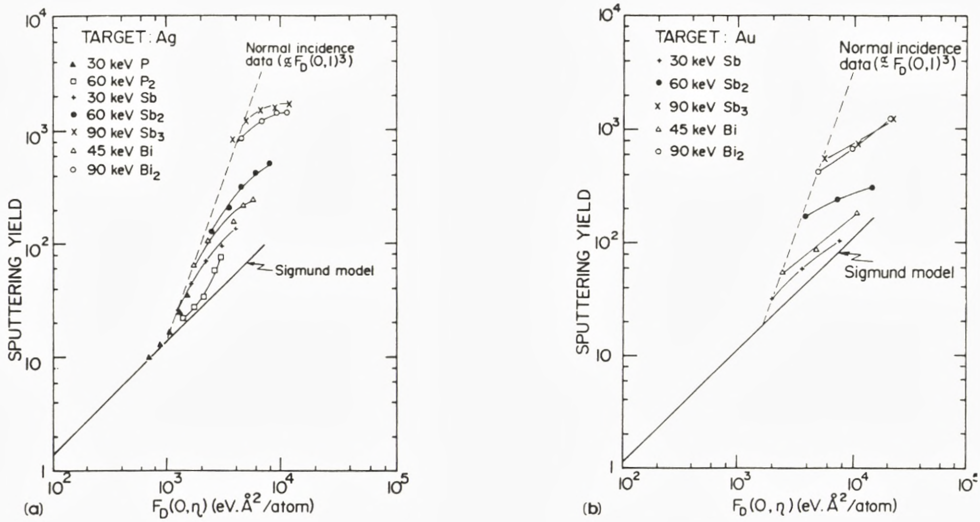

Figure 6. Measured sputtering yields of silver and gold bombarded with mono- and polyatomic ions at different energies and incidence angles as a function of surface-deposited energy, calculated by Monte Carlo methods. (From Thompson & Johar, 1981).

group have been treated in detail by Thompson (1980, 1981a,b). A number of his interpretations will be scrutinized in the discussion section below.

Hofer et al. (1983) mainly studied the influence of temperature on yield to be discussed below, but they also determined the silver yield from 100 keV Sb^+ and 200 keV Sb_2^+ impact. The enhancement factor (~ 1.5) is in good agreement with other experimental data.

Merkle & Jäger (1981) (see also their preliminary report, Jäger and Merkle (1978)) bombarded gold foils with 10 to 500 keV Bi^+ and Bi_2^+ ions and observed the foils by transmission electron microscopy (TEM). Some of their results are shown in Figs. 7 and 8. They observe craters in the surface of the foil and ascribe these craters to high-yield events. Within the resolution of the microscope only 1.5% of the incident Bi_2^+ ions at 100 keV/atom give rise to visible craters, but these craters contained some 40% of the sputtered atoms. Note also the facetted shape of the craters in fig. 7, a feature we shall return to in the discussion section. Fig. 8 shows the distribution of crater sizes. The yields from individual cratering events do of course scale as the crater volume, i.e. approximately with the third power of the diameter. The cutoff at low energy is related to an observational cutoff in the TEM. The figure is unique in the way that it constitutes the only published data set for fluctuations in sputtering yields. It illustrates that fluctuations are

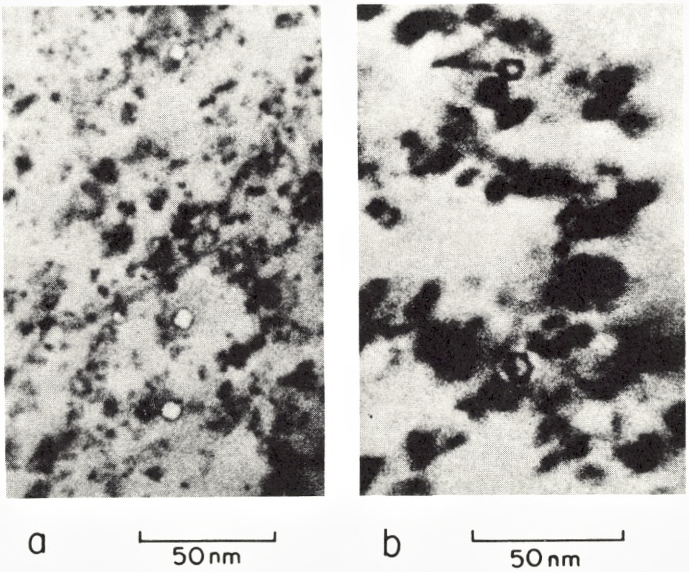

Figure 7. Faceted craters on a (100) Au surface (a) and a (111) surface (b) bombarded with Bi_2^+ ions. (From Merkle & Jäger, 1981).

substantially larger for dimer than for monomer irradiations. According to Merkle & Jäger (1981) this is thought to be related to the break-up of collision cascades into subcascades; a mechanism that will be more difficult under dimer than under monomer bombardment. If nonlinear effects exist for the system in question, they will be amplified by fluctuations, and the very large fluctuations may give some of the explanation for the large yield enhancement. Measurements of crater-size distributions are rather time-consuming. It is hence difficult to carry out systematic studies varying projectiles, targets and impact angles.

Beuhler & Friedman (1980, 1986) and Mathew et al. (1986) irradiated among other targets carbon with very large water clusters ($n \leq 150$) at 300 keV. Their results, partly also reported as TEM pictures, may to some extent be influenced by electronic energy deposition. It is interesting to note that yields are so large that the total ion energy is insufficient to atomize the sputtered carbon. Some of the TEM pictures by Mathew et al. from Pt-covered carbon look very much like the pictures published by Andersen et al. (1978) from Au-covered carbon foils bombarded with 15 MeV heavy ions, but there the irradiation conditions were clearly in the region dominated by electronic stopping.

A large number of papers (e.g. Hedin et al., 1989; Hunt et al., 1989; Thomas

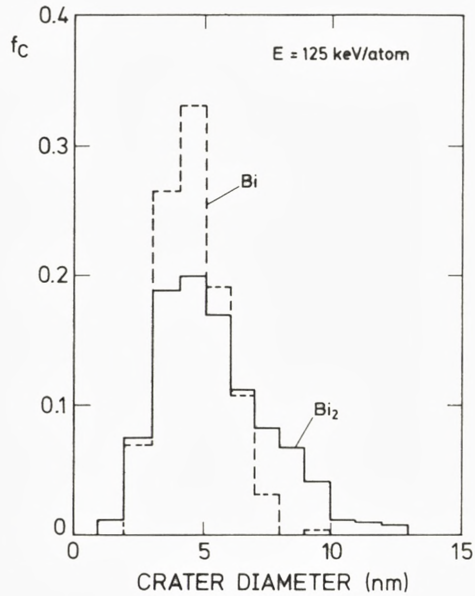

Figure 8. Crater size distributions for 125 keV Bi^+ and 250 keV bombardment of Au. (From Merkle & Jäger, 1981).

et al. 1985 and 1988; Salehpour et al., 1988 and 1989) report different sorts of yield enhancement under cluster bombardment in the electronic stopping region. Discussion of these results is considered to be outside the scope of the present review.

A particularly exciting cluster-enhanced yield involving nuclear collisions was introduced through the report of enhanced fusion rates under bombardment of metal targets with slow $(D_2O)_n$ clusters. (Beuhler et al., 1989, 1990, 1991). The results were heavily challenged experimentally (Fallavier et al. 1990, 1993; Vandenbosch et al., 1991, 1992) and finally withdrawn by the original authors (Beuhler et al., 1992). Meanwhile attention has been called to an interesting collision mechanism (Carraro et al., 1990) where a light atom (the deuteron) rattles to and fro between heavy atoms in the projectile cluster and the target (the so-called Fermi shuttle) and acquires a much larger energy than what might be transferred in a single collision, albeit with very low probability. The mechanism was not directly discussed by Sigmund in his 1989 review but implicitly present. Hautala et al. (1991) showed it to be incapable of explaining the yields originally published by Beuhler et al. (1989). The aspect which is interesting in this connection is whether

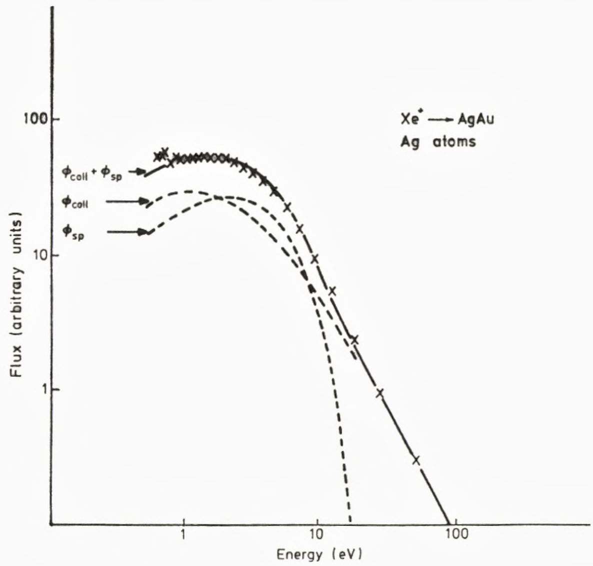

Figure 9. Energy spectra of silver atoms sputtered from an AgAu alloy by 6 keV Xe bombardment. A low energy spike component in the spectra is clearly seen. (From Szymonski et al., 1978).

the mechanism may give rise to sputtering effects. Sigmund (1989) suggests this may well be the case close to the sputtering threshold but experiments to confirm the idea will be difficult. Fallavier et al. (1993) find they are not able to lower their background sufficiently to measure fusion yields at the rate predicted by Hautala et al. and thus to confirm the feasability of the mechanism. They speculate whether other measurements might be performed. In spite of the possibility of making sputtering measurements, much more direct evidence appears to be obtainable from measurements of backscattering spectra, in particular because higher energy monomers or small-cluster beam-background components will have a lower scattering cross section than those looked for in contrast to what was the case for cluster-induced fusion. Pile-up in the spectra might, however, give rise to problems.

In the original paper on yield enhancement from dimers, Andersen & Bay (1974) concluded that if the enhancement was due to a spike mechanism, the 'extra' sputtered atoms must be expected to have very low energy. This prediction was tested through a measurement of the total reflected energy (also called sputtering efficiency), which is largely independent of surface-binding energy (Andersen, 1970). The experiment was performed with Se and Te monomers and dimers on lead. In spite of an expected yield enhancement of about a factor of 4 in the latter case, no enhancement in the reflected energy could be detected within the measuring accuracy of 10%. The extra sputtered atoms must hence have an average energy of only some percent of those sputtered by monomers. In spite of the fact that these results were reported in the original publication of nonlinear yields, they appear to have been largely forgotten.

Even more direct evidence for a low-energy component in the energy spectra of collisionally sputtered particles was presented later. Szymonski & de Vries (1977) bombarded Ag and Au with 6 keV Xe. Later (Szymonski et al. 1978) they also used an AgAu alloy as a target. Fig. 9 shows one of their energy spectra decomposed into a cascade part (fitting eq. (2) to the high energy part) and a low-energy Maxwell-Boltzmann-like part. From the cascade part surface-binding energies for the pure metals as well as the alloy components may be deduced. Ahmad et al. (1981) used 20 keV Ar and Xe on Ag[2]. While the spectrum found for Ar bombardment peaks at 2 eV, the maximum is found at 0.4 eV for xenon bombardment. Husinsky et al. (1978, 1980) used a very low binding energy target, viz. sodium. Again a clear low-energy spike component was seen. Measurements of velocity distributions of sputtered atoms in general were reviewed by Thompson (1987).

Oostra et al. (1988) performed an experiment that was the direct spectrum equivalent of the sputtering-efficiency measurement of Andersen & Bay (1974). They irradiated gold with 4 keV/atom iodine monomers and dimers. The spike component was, as expected, much stronger in the dimer than in the monomer case and a substantial yield enhancement was found. The surprising feature of the paper was, that through fits of a Maxwell-Boltzmann distribution to the low-energy part of the spectra, a higher temperature was deduced for the monomer than for the dimer case. A natural point of criticism would be that the model was strained too much through assuming a distribution corresponding to thermal equilibrium. Szymonski & Postawa (1990) showed that if the fit was instead made to the cascade part, the monomer spectrum showed a negative component at the lower energies. Szymonski & Postawa resolved the discrepancy by ascribing this artefact to a combination of uncertain background subtraction and very poor statistics for that part of the spectrum.

Closely coupled to a possible low-energy part of the energy spectra was the question of the influence of temperature on sputtering yields. In particular the very strong temperature dependence of noble-gas sputtering of silver found by Nelson (1965) was by many taken as clear evidence for spikes, until Besocke et al. (1982) and Hofer et al. (1983) showed that the temperature dependence was mainly due to background sublimation, not sputtering. Hofer et al. found only an approximate

[2]See also Ahmad et al. (1980) as another example of the work of M.W. Thompson and his group on sputtered energy spectra.

30% yield rise from 25°C to 775°C independent of whether irradiation was with 100 keV/atom Sb or Sb_2. In both the 1982 and 1983 publications the authors were very puzzled by the missing influence of target temperature on spike sputtering, but such evidence was also deduced from measurements of energy spectra from Cr and Ca by Husinsky et al. (1984, 1985). Sigmund & Szymonski (1984) showed from detailed analytical calculations that no strong influence should be expected, but that appears not to have influenced Hofer's viewpoint in his recent (1991) review on angular energy and mass distributions of sputtered particles.

Ion-induced electron emission is a phenomenon basically connected to the electronic stopping of the projectile ion although sometimes in a rather complicated way (Rothard et al. 1992). The question which has been raised several times is whether the much longer lifetime of the spike than that of the collision cascade proper will allow a sufficient coupling between atom and electron systems to cause enhanced electron emission. This hypothesis was tested by Thum & Hofer with V_n^+ and Nb_n^+ clusters ($n \leq 9$, $v < 4\times10^5$ m/s) incident on stainless steel. Absolutely no nonlinear effects were found. Other investigations (e.g. Hasselkamp & Scharmann, 1983; Kroneberger et al., 1989) showed molecular effects at much higher velocities. These are thought to be caused by nonlinearities in the electronic stopping.

Early results for enhanced ion yields from Si bombarded by Ne_2 and Ar_2 were published by Wittmaack (1979). Molecular effects on ion emission have also been studied more recently. While it is difficult to extract information relevant for the present purpose from the measurements of total emitted negative charge under $(H_2O)_n$ bombardment (Beuhler & Friedman, 1980, 1986) and from Reuter's (1987) measurements with CF_3^+ and O_2^+ irradiation, recent studies involving keV bombardment with $(CsI)_n^+$ and Au_n^+ (Blain et al., 1989; Benguerba et al., 1991) appear more promising. Firstly, their use of a liquid-metal ion source (LMIS) allows beams up to Au_5^+; presently only with energies up to approximately 30 keV, but when work to install a LMIS in a van de Graaff terminal will be finished shortly (Le Beyec, 1993) much higher energies and a much broader velocity region will be available. The LMIS has also been used successfully in a tandem accelerator, where the clusters have been transported through the charge-exchange system without breaking up (Schoppmann et al., 1993). This even further extends the energy range, still within the nuclear stopping region for heavy targets.

An example of the results of Benguerba et al. (1991) is shown as Fig. 10 displaying Au^- emission from gold bombarded with gold clusters. Very large enhancement factors are seen. For Au_4^+ at 10 keV/atom, a slight extrapolation of the data indicates a factor of 15. If the same enhancement factor holds for the total yield, that would bring the yield up to 300 for a 40 keV Au_4 cluster (c.f. fig. 1). If the involved atoms come out as single atoms – which they probably do not do – 30% of the incident energy would be consumed simply to overcome the sublimation energy.

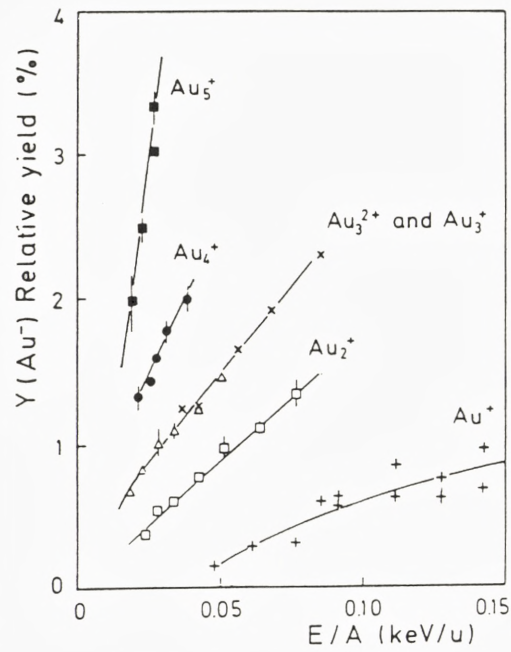

Figure 10. Au^- yield from a gold target as a function of primary ion energy per mass unit. The primary ions are Au_n^+ and Au_n^{++} with $n \leq 5$. (From Benguerba et al., 1991).

The question in such experiments is whether the ionization depends on the energy density of the spike. The Hofer & Thum results for electron emission discussed above indicate that not to be the case, but direct experimental evidence is entirely missing. Total yield measurements over a broad energy interval for Au_n impact on gold ought to be one of the first priorities when the new beams become available (della Negra et al., 1993, Demirev et al., 1991, Schoppmann et al., 1993, Le Beyec, 1993). A potential problem is to obtain mass and energy analyzed beams of heavy clusters. Beam lines are usually not equipped with bending magnets and focussing devices that allow handling of singly or doubly charged particles with masses of the order of 1000 to 2000 atomic mass units. It will be exceedingly difficult to measure absolute neutral sputtering yields on an event-by-event basis where the nature of the projectiles is identified by time-of-flight methods, which in other connections may be a convenient way to handle the indentification problem.

The Au-Au_2 negative ion yield enhancement factor at 15 keV/atom is found to be approximately 3.5. Johar & Thompson (1979) found the Bi-Bi_2 enhancement factor for the total gold sputtering yield to be 2.5 at 30 keV/atom and 3.9 at

45 keV/atom. This comparison seems to indicate that enhancement factors are substantially larger for Au^- ion yields than for total sputtering yields, further strengthening the case for measurements of both parameters.

Emission of clusters under cluster bombardment has been studied only on a few occasions. The crater measurements of Merkle & Jäger (1981) constitute circumstantial evidence for cluster emission but no direct proof. Beuhler & Friedman (1989) found emission of clusters up to C_{21}^+ from carbon bombarded with 240 keV $(H_2O)_{80}$ clusters and give detailed mass spectra, but similar spectra for single-molecule or small-cluster impact at the same energy per molecule are not available. Again, Benguerba et al. present interesting data. They conclude that 'cluster ions as projectiles are much more efficient than single atomic ions for ejecting complex secondary ions' a result that is in complete agreement with the circumstantial evidence from Merkle & Jäger. Further they conclude that 'our data support also a direct ejection mechanism of clusters under cluster impact'. This conclusion agrees well with the one reached by Andersen (1989) in his review of cluster emission in sputtering but less with the viewpoint of Hofer (1991) that tended to see sputtered clusters as created through a recombination mechanism. The two latter papers present general discussions of the field of cluster emission.

3 Computer Simulations

Simulations of sputtering through computer calculations were reviewed at length by Andersen (1987). It is not the idea here to repeat the classifications and conclusions of that paper nor to discuss any of the 400 references treated in the review. It is, however, amazing to note that virtually none of the papers discussed then treated cluster impacts in view of the number of papers on that subject that have appeared over the relatively short period since that review was completed.

The first group of papers treated here is concerned with cluster impact energies below the sputtering threshold: We are in the domain of cluster-beam deposition of films. The low energy makes possible rather detailed computer studies on small samples, but the general interest was very much triggered by the claim by Takagi & Yamada (1989) that the impact of large, ionized, low-energy clusters enhanced the epitaxial growth of high-quality crystal films. The claim was supported by the TEM observations of deposited discontinous films of Usui et al. (1989), but their films look very much like those described by Andersen et al. (1979) produced by simple evaporation. Silicon epitaxial deposition in particular was studied by Schneider et al. (1987) (not employing cluster impact), by Biswas et al. (1988) who gave some support for the Takagi conjecture and by Kwon et al. (1990) (the same group) who now were less enthusiastic. Kitazoe et al. (1984a,b) studied the impact of Al clusters on silicon and Cu on carbon. These programs were further developed by Yamamura (1990) for $(Ag)_n$ on carbon. In all cases the impacting clusters ($\sim$ 500 atoms and 6 - 10 eV/ atom) were found to flatten out on the substrate. No sputtering resulted. Xu et al. (1989) studied the impact of $(Ar)_n$ on Pt and found the impacting clusters to break up and individual atoms to be scattered nearly parallel to the surface. Hsieh & Averback (1990) and Averback et al. (1991) treated copper cluster impact on copper. At very low energy they found no particular effects from clusters. At higher energies, but still below the sputtering threshold, they found evidence for craters with a rim, rather like the pictures published by Mathew et al. (1986). Hence they saw no particular merit in large cluster beam deposition. Maybe that is rather fortunate as a closer inspection of the output of the Takagi source did not reveal the presence of large clusters in the beam (Brown et al., 1991).

A number of groups investigated cluster impacts on solids by means of computer simulations at energies where sputtering may occur. Molecular dynamics methods are used for the majority of these calculations. A Cambridge group looked at copper sputtering by $SiCl_4$ impact up to 1 keV (Park et al., 1987). Comparison to the yield of Ar atom impact showed no nonlinearities. For further details of their Ar sputtering studies, see also Stansfield et al. (1989). They returned to the $SiCl_4 \rightarrow$ Cu(001) case (Broomfield et al., 1990) using ab initio calculated interatomic potentials and now did find significant nonlinearities. Very large nonlinearities were found by Yamamura (1988) who investigated $(Ar)_n$ impact on carbon ($10 < n < 200$, $E = 100$ eV/atom) using a binary-collision code. The enhancement factor of the yield was 80 for the largest clusters. Very strong nonlinearities were also found for the energy deposition. It is relevant here to mention that Yamamura & Muramoto (1992) found the reflected energy to show a slight enhancement for $(Al)_{500}$ on Ag and $(Ag)_{500}$ on Al. These results did not include the energy of the sputtered atoms. One of the basic ideas of the spike concept was confirmed by the simulations of de la Rubia et al. (1987) and Averback et al. (1991). Energy deposition of up to 5 keV in Cu and Ni caused local melting lasting some picoseconds. Most spectacular in this connection was the formation of craters surrounded by a rim without sputtering or with very little sputtering as also discussed above.

Shapiro & Tombrello have published a series of papers on simulation of cluster sputtering starting in 1990 with 1 keV/atom impact of Al_{32} and Al_{63} on aluminium and gold. They found the target to be compressed substantially by the impact. Sputtering was seen, but nonlinearities in the yield might not be discerned. These results are presented in more detail by Shapiro & Tombrello (1991 a). In their next (1991 b) paper Au (100) and (111) targets were simulated, irradiated by monomer and dimer Kr, Xe, Au and U at perpendicular incidence at 5 keV/atom. Dimer yield enhancement factors larger than 1 were found in all cases, but they were smaller for the heavy than for the light projectile constituents. The authors suggest this to be due to saturation, since a substantial nonlinear effect was suspected to be present already for the monomer impact. This sounds like the experimental saturation effects suggested by Benguerba et al. (1991) as discussed above. The simulated energy spectra show the enhancement to occur at surprisingly high ejection energies (1-10 eV). Even processes with a rather high-energy threshold like core excitations may display cluster effects (Shapiro & Tombrello, 1992).

Finally a group of cluster impact papers by Sigmund and coworkers will be discussed. They are to a rather limited extent concerned with cluster sputtering effects (mostly not with sputtering at all). Nevertheless they raise a number of questions important for the problems discussed in the present paper. Shulga et al. (1989) introduced the tool of switching on and off the interaction between target particles (and also later between cluster constituents) in the simulation. Two important mechanisms are disclosed through this process: The clearing-the-way and blocking-the-way effects which give rise to decreased or increased energy deposition (as earlier pointed out by Yamamura, 1988). These effects are discomforting in the present connection. We have regarded the Sigmund (1969) sputtering theory a sort of benchmark from which to judge nonlinear effects in monatomic sputtering. This attitude reflected the idea that deposited surface energy was strictly proportional to the nuclear stopping powers and that the stopping power of cluster components were additive. At energies close to threshold it now looks as if nonlinearities may as well be attributed to the stopping power as to the sputtering process. In this region the situation turns out to be as complicated as it is in the electronic-stopping region. In Shulga & Sigmund (1990) penetration of gold clusters through silicon is treated. Here the clearing-the-way effect dominates and stopping powers are lowered. In Pan & Sigmund (1990) the opposite situation is treated: carbon clusters on gold targets. Energy deposition is additive but carbon atoms may appear with high energies. This becomes even more pronounced if the clusters are mixed light and heavy (Hautala et al., 1991). Here we see the Fermi shuttle clearly demonstrated through Monte-Carlo and molecular-dynamics simulations as discussed in connection with cluster-induced fusion processes. Shulga (1991) finds lowered stopping powers for Cu clusters on copper as do Shulga & Sigmund (1992) for copper clusters on gold. In the latter case sputter-yield enhancement factors lower than one were calculated. Maybe the experimental data of Oliva-Florio et al. (1979) (see fig. 5 here) should really be extrapolated downwards to enhancement factors lower than one?

Johannessen (1993) studied Au (100) sputtering by 250 eV Xe and 500 eV Xe_2. He found only slight nonlinear effects, but when the dimers were oriented with their axis perpendicular to the surface, the clearing-the-way effect showed up.

4 Discussion

The aim of the present section is not to discuss which spike model best fits the experimental data. Experimental data are not sufficient nor covering a large enough energy interval to allow such an evaluation. The idea is rather to have a critical look at other alternative models that have been aired to see whether any of those could explain the experimental observations. We are hence for a brief moment neglecting the fact that the success of linear sputtering theory for moderate energy-deposition densities implies that spike effects must play a role for high densities due to the breakdown of the assumptions of linear theory.

Thompson (1981 a,b) implied that the mesoscopic roughening of the surface topography caused by high-yield events could explain part of the yield enhancement. Experimentally, such roughening has been clearly demonstrated (see Carter et al. (1981) for a review). Thompson made reference to the calculations of Littmark & Hofer (1978) indicating an increase of yield with increased surface roughening. Experimentally, the yield increase was seen by Besocke et al. (1982). Note in this connection that plenty of other high-dose effects may change the yields (Andersen & Bay, 1972, 1973; Andersen 1984). Thompson's conjecture, however, neglects the main virtue of the measuring technique employed by Andersen and Bay (1974, 1975): As seen from fig. 4 (and all the other data published by these authors), the enhancement factor is measured by comparing monomer and dimer yields at identical surface conditions. The measured enhancement factors must, therefore, be totally independent of dose even if strong dose effects are found for individual yields. The model was hence experimentally untenable before it was even proposed.

Johar & Thompson (1979) proposed an effect caused by a lowering of U_s due to radiation damage. As discussed below, surface-binding energies will depend on exactly from which sites at the surface sputtering takes place. Sputtering-yield measurements have probably never been made from a perfect surface. In reality eq. (1) as well as eq. (2) should hence contain a distribution of surface binding sites. The surface roughening caused by high-energy-density events is probably not very different from that caused by low-yield events due to surface diffusion, as long as we look on the atomic scale. Under high-yield conditions sputtering may occur through a two-step process where an atom is first moved to a low-energy site and later – within the same cascade – sputtered. A possibility in question is local surface melting. Such two-step processes will enhance the yields. By definition they are of a nonlinear nature. They are not thought to be particularly important.

Many authors proposed that the sputtering of clusters would lower the surface binding energy to be overcome (e.g. Merkle & Jäger (1981) and Beuhler & Friedman (1980, 1989)). The proposal is qualitatively appealing but has not been evaluated quantitatively. If the clusters are assumed to be hemispherical, a lot

Table I

fcc surface	(111)	(100)
Atom on plane	3	6
Corner on overlayer	6	6
Atom on ledge	7	7
Aton im plane	9	8

of different high-index crystal surfaces will be generated, and it is not clear what the binding energy will be. Here we shall present a much simplified model which, however, is easily quantified.

Calculations will be presented for close-packed clusters emitted from the (111) and (100) surfaces of an fcc lattice. Surface binding energies will be assumed to be proportional to the number of nearest neighbours which the emitted configuration of atoms had to the lattice left behind. As the lattice will only relax to a very limited extent during the emission process, the assumption is presumably quite justified.

An atom in an fcc lattice has 12 nearest neighbours. They are distributed differently in the (111) and (100) planes. An atom has 6 nearest neighbours within the (111) plane and 3 below and above. Within the (100) plane there are 4 neighbours while 4 are found below and above. Hence an atom expelled from the (111) plane leaves 9 nearest neighbours behind while an atom leaving the (100) plane only leaves 8: The (111) plane is hence expected to have a higher binding energy than (100). Within the present context this agrees with the fact that Hofer et al. (1983) found a lower enhancement factor for sputtering from the gold (111) surface than from (100).

Considering non-perfect surfaces we find the number of neighbours shown in table 1. Let us now look at planar triangular clusters expelled from the (111) surface. Let the edge length be n, the number of atoms in the cluster N and the number of nearest neighbours NN. For this particular configuration we find $N = n(n+1)/2$ and $\mathrm{NN} = 3n(n+5)/2$. Note that neighbours not only are found at the edges but also in the plane below. Fig. 11 shows NN and NN/8N as a function of N, i.e. normalization is chosen to an atom within the (100) plane.

Similarly, for the (100) plane, we find $N = n^2$ and $\mathrm{NN} = 4n(n+1)$. In the limit of very large plates, we find NN/8N to be 0.5 for the (100) surface and 3/8 for the (111) surface as shown in Fig. 11.

We now consider triangular pyramids extending inwards from the (111) plane. Beneath a surface triangle with side length n is removed a triangle with side length $(n-1)$ etc. In total, a regular tetrahedron limited by (111) faces is cut out. After

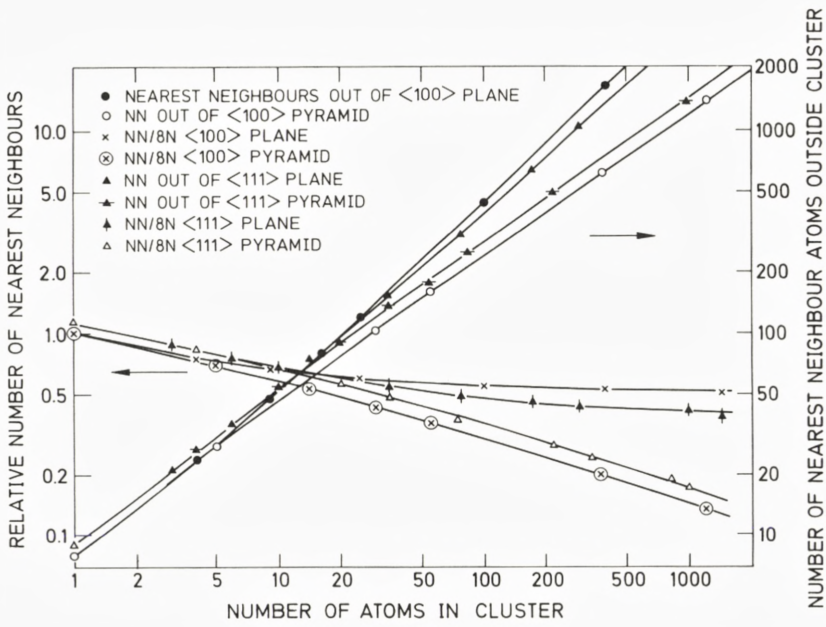

Figure 11. Nearest neighbours and relative number of neighbours of planar and pyramidal clusters from on (111) and (100) surfaces of an fcc lattice.

some calculations we find $N = n(n+1)(n+2)/6$ and $\mathrm{NN} = 9n(n+1)/2$. Note that a similar construction is not possible for an hcp lattice.

For the 4-sided pyramids on the (100) plane, we find $N = n(2n+1)(n+1)/6$ and $\mathrm{NN} = 2n(3n+1)$, again shown in Fig. 11. Again NN and NN/8N is shown as a function of N in fig. 11.

Note from the figure that significant differences between the surface energy saved for planar and volume clusters are not found before $N \geq 10$. Note also that the pyramids on the (100) face are ultimately the most energy-saving ones because their shape comes closer to a sphere than the (111) pyramids. Considering numbers, we note that a 2000 atom pyramid may be expelled at the cost of 200 individual emitted atoms.

The shapes postulated here are exactly the ones found for segregated inclusions in an fcc lattice (Johnson et al., 1992). They are also the shapes of the craters found by Merkle & Jäger (1981) as seen in fig. 8. This, however, does not tell whether the clusters were expelled in such a shape or whether the craters first obtained their equilibrium shape after the emission. Finally, it should be noted that the full lines of fig. 11 may not be used for interpolation. Intermediately-sized clusters will have binding energies above the lines because they must have a more regular shape. A similar argument for the continuum case has very recently been presented by Tersoff et al. (1993). Note that the abundance of clusters may not be judged either from time-of-flight or from laser fluorescence measurements of the energy spectra. In both cases energies per atom are measured. It is concluded that emission of clusters may play a non-negligible role for the high nonlinear yields. This is also related to the role played by fluctuations in the sputtering yields. If fluctuations are large, cluster emission will per se give rise to nonlinear yields, but both experimental and theoretical information is insufficient to judge this possibility.

As the last suggestion, Thompson (1981a,b) proposed that rather than considering the energy deposited within a thin layer at the surface, the energy deposited over the crater depth should be considered. He claims that if that be done, linear collision theory would still apply. It may be argued that if linear collision cascade theory gives the yields, it should also give the energy spectra and this is experimentally known not to be the case. Further, if it were, it might be shown that e.g. the 2000-atom yield found for 40 keV Bi_3 sputtering of gold would imply a kinetic energy of the sputtered atoms of some 70 keV with an average energy of 35 eV calculated from eq. (2). Hence the energy spectra must be different from eq. 2 simply because of energy conservation. Finally in standard linear collision cascade theory it is not possible to deplete a layer of atoms: There will always be a full layer to sputter from.

It is concluded that emission of clusters may play a non-negligible role in nonlinear effects but spike effects must carry the main load.

5 Conclusions and Recommendations

- Spike effects are the main cause for nonlinear effects in sputtering yields.
- Cluster emission may play a substantial role.
- The amount of existing systematic data does not allow to discern between different spike models.
- There is a substantial need for data on yields and energy spectra, to be taken over a very broad energy region with clusters containing different numbers of heavy atoms.
- The influence of spikes on the ionization probability (or electron attachment probability) should be studied.
- The influence of cluster impact on cluster emission should be studied.

References

Ahmad S, Farmery BW and Thompson MW, 1980: Nucl. Instrum. Methods **170**, 327

Ahmad S, Farmery BW and Thompson MW 1981: Phil. Mag. A **44**, 1387

Almen O and Bruce G, 1961: Nucl. Instrum. Methods **4**, 257

Andersen HH, 1970: Radiat. Eff. **3**, 51

Andersen HH, 1984: *Ion Implantation and Beam Processing.* eds. Williams JS and Poate JM, (Academic Press, Sydney) 127

Andersen HH, 1987: Nucl. Instrum. Methods **B18**, 321

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

Andersen HH and Bay HL, 1972: Radiat. Eff. **13**, 67

Andersen HH and Bay HL, 1973: Radiat. Eff. **19** 139

Andersen HH and Bay HL, 1974: J. Appl. Phys. **45**, 953

Andersen HH and Bay HL, 1975: J. Appl. Phys. **46**, 2416

Andersen HH and Bay HL, 1981: *Sputtering by Ion Bombardment. I.* ed. Behrisch R, (Springer, Berlin) 145

Andersen HH, Knudsen H and Møller Petersen P, 1978: J. Appl. Phys. **49**, 5638

Averback RS, Diaz de la Rubia T, and Hsieh H, 1991: Nucl. Instrum. Methods **B59/60**, 709

Balaji V, David, DE Maguera TF, Michl J and Urbassek HM, 1990: Nucl. Instrum. Methods **B46**, 435

Bay HL, Andersen HH, Hofer WO and Nielsen O, 1976: Nucl. Instr. Methods **132**, 301

Benguerba M, Brunelle A, Della Negra S, Depauw J, Joret H, leBeyec Y, Blain MG, Schweikert EA, Ben Assayag G, and Sudrane P, 1991: Nucl. Instr. Methods **B62**, 8

Besocke K, Berger S, Hofer WO, and Littmark U, 1982: Radiat. Eff. **66**, 35

Beuhler RJ and Friedman L, 1980: Nucl. Instrum. Methods **170**, 309

Beuhler RJ and Friedman L, 1986: Chem. Rev. **86**, 521

Beuhler RJ and Friedman L, 1989: Journ. de Physique **50**, C2, 127

Beuhler RJ and Friedman L, 1989: Phys. Rev. Letters **63**, 1292

Beuhler RJ and Friedman L, 1992: Phys. Rev. Letters **68**, 2101

Beuhler RJ, Chu YY, Friedländer G, Friedman L and Kunman W, 1990: J. Phys. Chem. **94**, 7665

Beuhler RJ, Chu YY, Friedländer G, Alessi JG, lo Destro V and Thomas JP, 1991: Phys. Rev. Letters **67**, 473

Biswas R, Grest GS and Soukoulis CM, 1988: Phys. Rev. **B38**, 8154

Bitensky IS and Parilis FS, 1987: Nucl. Instrum. Methods **B21**, 26

Blain MG, Della Negra S, Joret H, le Beyec Y and Schweikert EA, 1989: Phys. Rev. Letters **63**, 1625

Broomfield K, Stansfield RA and Clary DC, 1990: Surf. Sci. **227**, 369

Brown WL, Jarrold MF, McEachern RL, Sosnowski M, Takaoka G, Usui H and Yamada I, 1991: Nucl. Instrum. Methods **B59/60**, 182

Carraro C, Chen BQ, Schram S, and Koonin SE, 1991: Phys. Rev. **A42**, 1379

Carter G, 1979: Radiat. Eff. Letters **43**, 193

Carter G, Navinsek B and Whitton JL, 1981: *Sputtering by Particle Bombardment.II.* ed. Behrisch R, (Springer, Berlin) 232

David DE, Maguera TF, Tian R, Stulik D and Michl J, 1986: Nucl. Instrum. Methods **B14**, 378

de la Rubia T Diaz, Averback RS, Benedek R, and King WE, 1987: Phys. Rev. Letters **59** 1930

della Negra S, Brunelle A, le Beyec Y, Cureaudeau JM, Mouffron JP, Waast B, Håkansson P, Sundquist BUR and Parilis E, 1993: Nucl. Instrum. Methods **B74**, 453

Demirev P, Reimann CT, Axelson J, Kjellberg J, Håkansson P and Sundquist BUR, 1991: *Proc.Eighth Int.Conf. Secondary Ion Mass Spectrometry (SIMS VIII)*, eds. Benninghoven et al. (Wiley, Chichester), 33

Fallavier M, Kemmler J, Kirsch R, Poizat J-C, Remillieux J and Thomas J-P, 1990: Phys. Rev. Letters **65**, 621

Fallavier M, Kirsch R, Poizat J-C, Remillieux J, Rothard H and Thomas J-P, 1993: Phys. Rev. Letters **70**, 1022

Grønlund F and Moore JW, 1960: J. Chem. Phys. **32**, 1540

Harrison MR and Edwards PP, 1985: *The Metallic and Non Metallic States of Matter*, eds. Edwards, PP and Rao, NR, (Taylor and Francis, London), 389

Hasselkamp D and Scharmann A, 1983: Phys. Letters **96A**, 259

Hautala M, Pan Z and Sigmund P, 1991: Phys. Rev. **A44**, 7428

Hayashi C, 1987: Physics Today **44**

Hedin A, Håkansson P, Sundquist BUR and Johnson RE, 1989: Journ. de Physique **50**, C2, 215

Hofer WO, 1991: *Sputtering by Particle Bombardment III*, eds. Behrisch R and Wittmaack K, (Springer, Berlin-Heidelberg) 15

Hofer WO, Besocke K and Stritzker B, 1983: Appl. Phys. **A30**, 83

Hunt JE, Salehpour M, Fishel DL and Tou JC, 1989: Jour. de Physique 50, **C2**, 27

Hsieh H and Averback R, 1990: Phys. Rev. **B42**, 5365

Husinsky W, Bruckmüller R, Blum P and Viehböck F, 1978: Natl. Conf. *Interaction of Atomic Particles with Solids* (Minsk, USSR)

Husinsky W, Bruckmüller R and Blum P, 1980: Nucl. Instrum. Methods **170**, 287

Husinsky W, Betz G, and Girgis I, 1984: J. Vac. Sci. Technol. **A2**, 698

Husinsky W, Betz G and Girgis I, 1985: J. Vac. Sci. Technol. **B3**, 1543

Jäger W and Merkle K L, 1978: *Proc.Ninth Int.Conf.Electron Microscopy*, (El.Micr.Soc. Canada, Toronto) 378

Johannessen K, 1993: Nucl. Instrum. Methods **B73**, 481

Johar SS and Thompson DA, 1979b: Surf. Sci. **90**, 319

Johnson E, Hjemsted K, Schmidt B, Bourdelle KK, Johansen A, Andersen HH and Sarholt-Kristensen L, 1992a: Mat. Res. Soc. Symp. Proc. **235**, 485

Johnson E, Hjemsted K, Schmidt B, Bourdelle KK, Johansen A, Andersen HH and Sarholt-Kristensen L, 1992b: Electron Microscopy **2**, 267

Johnson RE, 1987: Int. J. Mass Spect. Ion Phys. **78**, 351

Johnson RE and Schou J, 1993: Mat. Fys. Medd. Dan. Vid. Selsk. **43** 403

Kitazoe Y and Yamamura Y, 1980: Radiat. Eff. Letters **50**, 39

Kitazoe Y, Sano M, Yamamura Y, Furutani H, and Yamamoto K, 1984a: Phys. Rev. **C29**, 828

Kitazoe Y, Gyalassi M, Daneilewicz P, Toki H, Yamamura Y, and Sano M, 1984b: Phys. Letters **B138**, 854

Kofmann R, Cheyssac P and Garrigos R, 1990: Phase Transitions **24-26**, 283

Kroneberger H, Rothard H, Burkhard M, Kemmler J, Koschar P, Heil O, Biedermann C, Leucinas S, Keller N, Lorenzen P, Hoffmann D, Clouvas A and Veje E, 1989: Journ. de Physique **50**, C2, 99

Kwon I, Biswas R, Grest GS and Soukoulis CM, 1990: Phys. Rev. **B41**, 3678

Le Beyec Y, 1993: Private communication

Littmark U and Hofer WO, 1978: J.Mater.Sci. **31** 2577

Matthew MW, Beuhler RJ, Ledbetter M and Friedman L, 1986: Nucl. Instrum. Methods **B14**, 448

Merkle KL and Jäger W, 1981: Phil. Mag. **44**, 741

Merkle KL and Pronko PP, 1974: J. Nucl. Mater. **53**, 231

Nelson RS, 1965: Phil. Mag. **11**, 291

Oliva-Florio AR, Alonso EV, Baragiola RA, Ferron J and Jakas MM, 1979: Radiat. Eff. Letters **50**, 3

Oliva-Florio A, Baragiola RA, Jakas MM, Alonso EV and Ferron J, 1987: Phys. Rev. **B35**, 2198
Oostra DJ, van Ingen RP, Haring A, deVries AE and Saris FW, 1988: Phys. Rev. Letters **61**, 1392
Pan Z and Sigmund P, 1990: Nucl. Instrum. Methods **B51**, 344
Park SC, Stansfield RA, and Clary DC, 1987: J. Phys. D: Appl. Phys. **20**, 880
Pelletier JD, Shapiro MH and Tombrello TA, 1992: Nucl. Instrum. Methods **67**, 296
Reuter W, 1987: Anal. Chem. **59**, 2081
Rol PK, Fluit JM and Kistemaker J, 1960: Physica **26**, 1000
Rothard H, Schou J, Koschar P and Groeneveld K-O, 1992: Nucl. Instrum. Methods **B69**, 154
Salehpour M, Fischel DL and Hunt JE, 1988: Phys. Rev. **B38**, 12320
Salehpour M, Fischel DL and Hunt JE, 1989: Journ. de Physique **50**, C2, 155
Schneider M, Schuller IK and Rahman A, 1987: Phys. Rev. **B36**, 1340
Schoppmann Ch, Wohlfart P, Brandl D, Saner M, Tamaschko CH, Voit H, Boussofiane K., Brunelle A, Chaurand P, Depauw J, Della-Negra S, Håkansson P and leBeyec Y., 1993: Nucl. Instrum. Methods (in press)
Schou J, Ellegaard O, Pedrys R and Sørensen H, 1992: Nucl. Instrum. Methods **B65**, 173
Shapiro MH and Tombrello TA, 1990: Phys. Rev. Letters **65**, 92
Shapiro MH and Tombrello TA, 1991a: Nucl. Instrum. Methods **B58**, 161
Shapiro MH and Tombrello TA, 1991b: Nucl. Instrum. Methods **B62**, 35
Shapiro HH and Tombrello TA, 1992: Nucl. Instrum. Methods **B66**, 317
Shulga VI, 1991: Nucl. Instrum. Methods **B58**, 422
Shulga VI and Sigmund P, 1990: Nucl. Instrum. Methods **B47**, 236
Shulga VI and Sigmund P, 1991: Nucl. Instrum. Methods **B62**, 23
Shulga VI, Vicanek M and Sigmund P, 1989: Phys. Rev. **A39**, 3360
Sigmund P, 1969: Phys. Rev. **184**, 383
Sigmund P, 1974: Appl. Phys. Letters **25**, 171
Sigmund P, 1975: Appl. Phys. Letters **27**, 52
Sigmund P, 1977: *Inelastic Ion Surface Collisions*, eds. Tolk NH et al. (Academic Press, New York) 121
Sigmund P, 1981: *Sputtering by Particle Bombardment I.*, ed. Behrisch R, (Springer, Berlin-Heidelberg) 9
Sigmund P, 1987: Nucl. Instrum. Methods **B27**, 1
Sigmund P, 1989: Journ. de Physique **50**, C2, 175
Sigmund P, 1993: Mat. Fys. Medd. Dan. Vid. Selsk. **43** 7
Sigmund P and Claussen C, 1981: J. Appl. Phys. **52**, 990
Sigmund P and Szymonski M, 1984: Appl. Phys. **A33**, 141
Stansfield RA, Broomsfield K and Clary CL, 1990: Phys. Rev. **B39**, 7680
Szymonski M, 1984: Nucl. Instrum. Methods **B2**, 583
Szymonski M. and de Vries AE, 1977: Phys. Letters **63A**, 359
Szymonski M and Postawa Z, 1990: Appl. Phys. **A50**, 269
Szymonski M, Bhattacharya RS, Overeijnder H and de Vries AE, 1978: J. Phys. D: Appl. Phys. **11**, 751
Takagi T and Yamada I, 1989: *Ion Beam Assisted Film Growth*, ed. Itoh T, (Elsevier, Amsterdam) 253
Tersoff J, Denier van der Gon, AW and Tromp RM, 1993: Phys. Rev. Letters **70**, 1143
Thomas JP, Filpus-Myuckx PE, Fallavier M and Schweikert EA, 1985: Phys. Rev. Letters **55**, 103
Thomas JP, Oladipo A and Fallavier M, 1988: Nucl. Instrum. Methods **B32**, 354
Thompson DA, 1980: *Proc.Symposium on Sputtering*, eds. Varga P et al. (Inst.allgem.Physik, Wien) 62

Thompson DA, 1981a: Radiat. Eff. **56**, 105
Thompson DA, 1981b: J. Appl. Phys. **52**, 983
Thompson DA and Johar SS, 1979: Appl. Phys. Letters **34**, 342
Thompson DA and Johar SS, 1981: Radiat. Eff. **55**, 91
Thompson MW, 1968: Phil. Mag. **18**, 377
Thompson MW, 1987: Nucl. Instrum. Methods **B18**, 411
Thum F and Hofer WO, 1979: Surf. Sci. **90**, 331
Townsend P D, 1983: *Sputtering by Particle Bombardment II.*, ed. Behrisch R, (Springer, Berlin-Heidelberg) 147
Urbassek HM and Michl J, 1987: Nucl. Instrum. Methods **B22**, 480
Usui H, Tanaka M, Yamada I and Takagi T, 1989: Nucl. Instrum. Methods **B37/38**, 886
Vandenbosch R, Trainor TA, Will DI, Neubauer J and Brown I, 1991: Phys. Rev. Letters **67**, 3567
Vandenbosch R, Ye D, Neubauer J, Will DI and Trainor T, 1992: Phys. Rev. **A46** (1992) 5741
Wittmack K, 1979: Surf. Science **90**, 557
Xu Guo-Qin, Holland RJ, Bernasek SL and Tully JC, 1989: J. Chem. Phys. **90**, 3831
Yamamura Y, 1988: Nucl. Instrum. Methods **B33**, 493
Yamamura Y, 1990: Nucl. Instrum. Methods **B45**, 707
Yamamura Y and Muramato M 1992: Phys. Rev. Letters **69**, 1463
Zalm PC and Beckers LJ, 1984: Philips Journ.Res. **39**, 11