

SURFACE SCIENCE LETTERS

**ENERGY COST TO SPUTTER AN ATOM FROM A SURFACE
IN keV ION BOMBARDMENT PROCESSES**

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We propose that the energy cost to remove one atom from the surface during ion bombardment is larger than the surface binding energy or bulk heat of sublimation. It is this value of the energy cost that is appropriate for use in analytic models of the sputtering process.

Over the years several analytic models [1–3] and computer simulations [4–10] have been proposed to describe processes which occur subsequent to the ion bombardment of solids. A critical piece in all of these models is the magnitude of the attractive interaction of an atom with a solid, a quantity referred to as the surface binding energy U . As a matter of convenience (and lacking a better choice) the value of the surface binding energy is often equated to the heat of sublimation of the solid, ΔH_s .

In the analytic models two experimentally measurable quantities are proposed to depend directly on the magnitude of the surface binding energy of an

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atom in the solid. One is the absolute yield of particles ejected [3]. That is, the more tightly bound an atom is to the solid, the less likely it is to eject. The other measurable quantity is the position of the peak in the energy distribution of the ejected particles [1]. In contrast to, for example, thermal desorption experiments where the peak position in the energy distribution is proportional to the temperature at which the atoms desorb from the surface, the analytic model of Thompson [1] predicts that the peak position should occur at U/n , where n is approximately equal to 2. This prediction regarding the value for the peak in the energy distribution arises from the energy distribution of moving atoms in the solid and the assumption that an atom must overcome a planar surface potential in order to escape. The perpendicular component of energy is reduced by an amount U and a peak results in the final energy distribution. This attractive interaction also indirectly effects other observables such as angular distributions.

The choice of ΔH_s for the energy parameter in the prediction of the sputtering yields gives reasonable agreement with the measured quantities [3], and for many years it has been thought that the Thompson equation fits the experimental energy distribution data quite well. However, Husinsky [11] has pointed out that the values of U fit to experimental energy distributions are sometimes larger than heats of sublimation of the materials. In this note, we propose that the measured peaks in the energy distributions actually occur at a value greater than $\Delta H_s/2$, and that this systematic deviation arises because the true energy cost to remove an atom from the solid is greater than ΔH_s .

There are several pitfalls in measuring the energy distribution of sputtered particles, extracting the peak position and then correlating this value to the appropriate one in the analytic models. First the peak region is quite broad and unless the statistics in the experiment are high it is difficult to determine the exact peak position. Second, usually only one component of the energy distribution is measured for particles ejected in off-normal directions from the crystal. The Thompson model predicts that the peak in the energy distribution of the component perpendicular to the surface occurs at $U \cos^2\theta/2$, where θ is the polar angle measured with respect to the surface normal [11,12]. In many experiments the measured distribution is an average over a finite solid angle of ejected particles. Not all workers are careful to state clearly which energy they are measuring and which energy they are comparing to theory. Bay, Berres and Hintz (BBH) have made this correction for particles nominally ejected perpendicular to the surface [13]. Another related effect just recently noted is that the peak in the total energy distribution shifts to a lower value as the take-off angle becomes more grazing [14]. This compounds the problem in finding an appropriate U value in experiments where the energy distribution is measured at a polar angle of 45° . In table 1, we have summarized some of the recent experiments on measuring the energy distributions of ground state atoms sputtered from clean metal surfaces.

As seen in table 1 the values of U extracted from sputtered atom energy distributions are larger than experimental values of ΔH_s except for Ca [23] and Ti [21]. The tabulated values of U for Ca [23] and Cr [24] should be larger than in table 1 if one accounts for the effect reported by Baxter et al. [14] which shows that the peak energy at a polar angle of 45° is 20% smaller than for normal ejection. The Argonne group (entries Fe [26], Zr [29] and U [27]) usually just assumed that $U = \Delta H_s$ in fitting their data to the theoretical curves.

Our contention is that the energy cost to remove an atom from a solid is actually greater than the heat of sublimation. The roots of this idea lie in two virtually unnoticed papers by Jackson [15,16]. He simulated the ejection of a surface atom by giving it an initial kinetic energy. The final kinetic energy (for a pairwise additive potential approximation) corresponds to an energy loss greater by 30%–40% than the bulk heat of sublimation. One would think that

Table 1

Element	ΔH_s ^{a)} (eV)	E_p ^{b)} (eV)	U ^{c)} (eV)	$U/\Delta H_s$	Ref.
Al	3.4		3.6	1.1	[21] ^{d)}
Ba	1.8	1.0	2.1	1.1	[22] ^{e)}
Ca	1.8		1.3	0.7	[23] ^{f)}
Cr	4.1		4.2–4.4	> 1.0	[24] ^{f,g)}
Fe	4.3	2.1	5.0	1.2	[25] ^{h)}
Fe	4.3		4.3 ⁱ⁾	1.0	[26]
In	2.5	2.4 ^{j)}	4.8	1.9	[14]
Rh	5.8	4.8 ^{j)}	9.6	1.7	[14]
Ti	4.9		4.6	0.9	[21] ^{d)}
U	5.4		5.4 ^{k)}	1.0	[27]
Zr	6.3		8.0	1.3	[28] ^{l)}
Zr	6.3		6.3 ^{k)}	1.0	[29]

a) Experimental atomization energies from ref. [20].

b) Raw peak position from the sputtering data in the cases where we have determined U .

c) Value to use in the equations of refs. [1–3] as taken from the experimental energy distribution curves. This is presumably the energy cost to remove an atom. In principle, this value, according to the Thompson model, should be twice E_p . Any deviations from this will be noted.

d) Author applied BBH correction.

e) Taken from fig. 3a, curve 8 in ref. [22]. We have applied the BBH correction.

f) These data were taken at a polar angle of 45° and no correction was made for the effect observed by Baxter et al. [14] where the peak shifts with polar angle.

g) The values reported here are the latest ones. Husinsky et al. [24] have shown that the peak position in the Cr energy distribution is strongly dependent on the carbon coverage.

h) We approximated the BBH correction.

i) The BBH correction should be small in this case.

j) The value of E_p is for the $\theta = 0^\circ$ curve.

k) Authors assumed the literature value of ΔH_s for U .

l) Authors applied the BBH correction so we have included their value for U .

this would imply that by ripping the entire solid apart it would take more energy than it had in the first place.

This dilemma is best described by examining a diatomic molecule which has a bond strength of D_e . Under the rules used for solids, the binding energy of each atom is $D_e/2$. If, however, one atom is clamped fixed and one asks how much kinetic energy must be supplied to the other atom so that the bond can be ruptured, then the answer is D_e – twice the “binding energy”. (Note that it now “costs” nothing to remove the second atom.) An analogous situation occurs in the solid. In one extreme in the ion bombardment process all atoms but one are fixed. The energy cost for this atom to escape the solid is larger than the heat of sublimation or surface binding energy. The appropriate value of U then is greater than ΔH_s in line with recent experimental results. It is not clear either theoretically or experimentally precisely what is the value of the energy cost to remove an atom from a solid. It is also not clear what influences the magnitude of this energy cost. Should it be the same for amorphous Rh, Rh{111}, Rh{110} and Rh{100}, for example?

The question still remains as to why computer simulations [5,8], which should describe the dynamics properly, predict a peak in the energy distribution at $\sim 0.4\Delta H_s$. This feature is a consequence of the assumption of pairwise additive potentials for the attractive portion of the interaction. The resulting potential in the surface plane is very rough with the surface atom positioned in a narrow potential well [17]. According to Jackson [15,16] the peak in the energy distribution, within the pair potential model, should occur at $\sim (1.4\Delta H_s)/2$ or $\sim 0.7\Delta H_s$. Except for ejection of the atom almost perpendicular to the surface all directions of ejection involve a collision with another surface atom. Consequently, there is an additional energy loss mechanism besides overcoming the attractive potential and *coincidentally* the peak position moves to a lower energy. Computer simulations in progress [17] using a many-body embedded atom [18] potential which is smoother in the surface region predict that the peak in the Rh{111} energy distribution occurs at $\sim (0.6-0.8)\Delta H_s$.

The concept presented here is that the energy cost to remove one atom from the surface during ion bombardment is larger than the surface binding energy or bulk heat of sublimation. It is this value of the energy cost that is appropriate for use in analytic models that help to quantify the observables from the sputtering process. Of note is that for energy distributions, corrections for the solid angle of collection (e.g. BBH [13]) are necessary. Similarly, the shift in the peak of the energy distribution with polar angle [14] must be considered when interpreting experimental data and correlating it to theory.

Note added. After submission of this manuscript, R. Kelly sent us two manuscripts dealing with the same concept for metals and metal oxides [19].

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References

- [1] M.W. Thompson, *Phil. Mag.* 18 (1968) 377.
- [2] B.J. Garrison, *Nucl. Instr. Methods B17* (1986) 305.
- [3] P. Sigmund, *Phys. Rev.* 184 (1969) 383.
- [4] D.E. Harrison, Jr., P.W. Kelly, B.J. Garrison and N. Winograd, *Surface Sci.* 76 (1978) 311.
- [5] B.J. Garrison, N. Winograd and D.E. Harrison, Jr., *Surface Sci.* 87 (1979) 101.
- [6] B.J. Garrison and N. Winograd, *Science* 216 (1982) 805.
- [7] N. Winograd, *Progr. Solid State Chem.* 13 (1982) 285.
- [8] M.H. Shapiro, P.K. Haff, T.A. Tombrello, D.E. Harrison, Jr. and R.P. Webb, *Radiation Effects* 89 (1985) 234.
- [9] M.T. Robinson and O.S. Oen, *Phys. Rev.* 132 (1963) 2385.
- [10] J.B. Gibson, A.N. Goland, M. Milgram and G.H. Vineyard, *Phys. Rev.* 135 (1964) A1780.
- [11] W. Husinsky, *J. Vacuum Sci. Technol.* B3 (1985) 1546.
- [12] G. Carter, G. Fischer, R. Webb, S. Dzoiba, R. Kelly and O. Auciello, *Radiation Effects* 45 (1979) 45.
- [13] H.L. Bay, W. Berres and E. Hintz, *Nucl. Instr. Methods* 194 (1982) 555.
- [14] J.P. Baxter, J. Singh, G.A. Schick, P.H. Kobrin and N. Winograd, *Nucl. Instr. Methods B17* (1986) 300.
- [15] D.P. Jackson, *Radiation Effects* 18 (1973) 185.
- [16] D.P. Jackson, *Can. J. Phys.* 53 (1975) 1513.
- [17] B.J. Garrison, N. Winograd, D. Lo, T.A. Tombrello, M.H. Shapiro and D.E. Harrison, Jr., in preparation.
- [18] M.S. Daw and M.I. Baskes, *Phys. Rev. Letters* 50 (1983) 1285;
S.M. Foiles, M.I. Baskes and M.S. Daw, *Phys. Rev.* B33 (1986) 7983.
- [19] R. Kelly, *Nucl. Instr. Methods B18* (1987) 388;
G. Falcone, R. Kelly and A. Oliva, *Nucl. Instr. Methods B18* (1987) 399.
- [20] *CRC Handbook of Chemistry and Physics*, 59th ed., Ed. R.C. Weast (CRC Press, Boca Raton, 1978).
- [21] E. Dullni, *Nucl. Instr. Methods B2* (1984) 610.
- [22] D. Grischkowsky, M.L. Yu and A.C. Balant, *Surface Sci.* 127 (1983) 315.
- [23] W. Husinsky, G. Betz and I. Girgis, *J. Vacuum Sci. Technol.* A2 (1984) 698.
- [24] W. Husinsky and G. Betz, *Nucl. Instr. Methods B15* (1986) 215;
W. Husinsky, P. Wurz, B. Strehl and G. Betz, *Nucl. Instr. Methods B18* (1987) 452.
- [25] B. Schweer and H.L. Bay, *Appl. Phys.* A29 (1982) 53.
- [26] C.E. Young, W.F. Callaway, M.J. Pellin and D.M. Gruen, *J. Vacuum Sci. Technol.* A2 (1984) 693.
- [27] R.B. Wright, M.J. Pellin and D.M. Gruen, *Nucl. Instr. Methods* 182/183 (1981) 167.
- [28] W. Berres and H.L. Bay, *Appl. Phys.* A33 (1984) 235.
- [29] M.J. Pellin, R.B. Wright and D.M. Gruen, *J. Chem. Phys.* 74 (1981) 6448.