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Prediction of the apex angle of surface cones on ion-bombarded crystalline materials

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Different methods of calculation based on ion channelling in a target matrix have been applied to the computation of the apex angle of surface conical shapes derived from ion bombardment. Comparison with values obtained experimentally by electron microscopy and deduced from sputter yield curves in the energy range 0.2 to 27.0 keV indicate that reasonable agreement can be achieved using a smeared Thomas Fermi atomic plane potential.

1. Introduction

Many publications have reported the formation of conical surface shapes appearing on both amorphous and crystalline materials subjected to ion etching. The phenomenon is independent of the type of impinging ion whether it be inert gas or metal ion. A recent paper has described and illustrated by scanning electron microscopy the development of surface cone structures on austenitic 18/8 stainless steel which had been bombarded by low energy argon ions [1]. The purpose of the present paper is to attempt to predict the cone apex angle for steel and other crystalline materials given the basic bombardment parameters from published sputtering data. The lower energy range is considered in detail since this is the region generally commercially utilized for cleaning and polishing surfaces, and employed by electron microscopists for ion-beam thinning of specimens.

2. Theoretical discussion

The cone apex angle, α_c, has been shown experimentally and by calculation [2, 3] to be given by the relationship

$$\alpha_c = 180° - 2\hat{\theta} \qquad (1)$$

where $\hat{\theta}$ is the angle of incidence of the incoming ion with the target surface for which the sputter yield curve gives a maximum value. The angle $\hat{\theta}$ is generally believed to be that critical angle beyond which the incoming ion has a probability of being reflected from the potential barrier presented by the surface plane of target atoms. As the value of $(\theta - \hat{\theta})$ increases, both ion penetration and the sputter yield of the target rapidly decrease. Such a case of ion reflection can be considered somewhat analogous to channelling where for an angle greater than a given angle of incidence to a plane or string of atoms, the moving atom or ion will not penetrate through the row of atoms. The ion will consequently be channelled along a given direction. This type of behaviour has been widely documented in sputtering experiments for both low and higher energy cases [4, 5]. A treatment for cone structures based on channelling, however, does ignore other possible processes. These processes may occur singly or simultaneously and embrace such effects as surface diffusion, binding energy fluctuations over the surface and redeposition of sputtered material [1].

Lindhard has published a paper on a theoretical approach to problems concerning directional effects for energetic charged particles moving through a solid [6]. Expressions can be derived for $\hat{\theta}$ from this work and hence cone angle values can be calculated. These can then be compared with values determined experimentally by electron microscopy or indirectly from sputter yield curves where $\hat{\theta}$ is substituted in Equation 1. For clarity, values obtained both directly and indirectly will be referred to as measured values. A number of different possible calculations to predict surface cone angles will be described briefly below. The first derivation will be considered in some detail since some incorrect forms of it have been given in the literature.

(1) This case considers the incidence of incoming particles nearly parallel to a plane of atoms in a lattice, but not travelling in any preferred direction with respect to the lattice. The potential of the target lattice atoms can be assumed smeared out to form a continuous planar potential $Y(z)$ if the distance of closest approach of the ion to a target atom or plane is not too great; z is the distance of the ion from the plane. For stainless steel etched with 0.3 keV argon ions, this approximation is easily satisfied since $r \approx 2a_0$ (alternately, $9a$) where a, the Thomas Fermi screening radius, is given by $(0.8853a_0)/(Z_1^{2/3} + Z_2^{2/3})^{\frac{1}{2}}$; a_0 is the Bohr radius of 0.53 Å and Z_1 and Z_2 are the atomic number of the incident ion and the target atom respectively. The potential as a function of the distance z from the plane is given by

$$Y(z) = n^{2/3} \int_0^\infty 2\pi r \, \mathrm{d}r V\sqrt{(z^2 + r^2)} \qquad (2)$$

n is a structure factor, the number of ions per unit cell; $r^2 = x^2 + y^2$ is the average distance parallel to the plane. $V(R)$, the ion-atom potential for a separation R, is of the form $(Z_1Z_2/R)\ \psi_0(R/a)$ where $\psi_0(R/a)$ is the Fermi function corresponding to an isolated atom [7, 8].

In the surface plane, i.e. $z = 0$, the potential takes the finite value of

$$Y(0) = \pi Z_1 Z_2 e^2 n^{2/3} \bar{R} \qquad (3)$$

where e is the electronic charge and $\bar{R}$ is the average radius of the atom. $\bar{R} = 2Ca = 3.46a$ if C, the constant of integration involved in the calculation, is equivalent to $\sqrt{3}$. This value is found to yield good over-all agreement. For large r/a, however, the value of C will take a slightly higher value.

From transverse energy and collision time considerations, the minimum distance of approach of an ion of energy E to a surface target atom is determined by the relation

$$Y(0) = E \sin^2\psi \qquad (4)$$

where ψ, the angle between the ion direction and the lattice plane, is given in sputtering notation by $\psi = 90° - \hat{\theta}$. Equation 4 assumes that the deflection in the single collision is smaller than the total scattering angle. If the angle ψ is larger, $\sin\psi$ should be replaced by $2 \sin \psi/2$, but for the angles considered here negligible error is incurred if this is ignored. To a first approximation, ψ can be written as

$$\psi = \left[\frac{Y(0)}{E}\right]^{\frac{1}{2}} \qquad (5)$$

$$= \frac{180}{\pi}\left[\frac{6.126\pi a_0^2 n^{2/3} Z_1 Z_2 E_{\mathrm{R}}}{(Z_1^{2/3} + Z_2^{2/3})^{\frac{1}{2}} E}\right]^{\frac{1}{2}} \qquad (6)$$

where e has been replaced by the Rydberg energy E_{R} through the relation $e^2 = 2a_0E_{\mathrm{R}}$ [9]. All the following formulae, as Equation 6 above, will give angles in degrees.

Since the continuous planar potential barrier of the plane is generally not higher than $Y(\text{eff}) = Y(0)/2$. The angle of incidence for the sputter yield maximum can thus be written as

$$\hat{\theta} = 90° - 347\left[\frac{n^{2/3} Z_1 Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{\frac{1}{2}} E}\right]^{\frac{1}{2}} \cdot \qquad (7)$$

This is essentially the expression quoted by Stewart and Thompson [2], but with a square root in the denominator and a factor 347 instead of 443.

For quite low values of E/E_{P} where

$$E_{\mathrm{P}} = \frac{Z_1 Z_2 e^2}{2\pi C^3 a^3 n^{2/3}} \qquad (8)$$

the barrier becomes somewhat lower. As

$$\frac{E}{E_{\mathrm{P}}} \propto \frac{E}{Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{\frac{1}{2}}} \qquad (9)$$

this quantity is only large for E large and/or Z_1Z_2 small. At the lower energy bombardment range, therefore, for example 0.3 keV argon etching of steel, $E/E_{\mathrm{P}} = 7 \times 10^{-4}$ and hence one would expect a somewhat smaller multiplication factor than 347 in Equation 7. The extent of this reduction, however, is not known. Thus for the present calculations, Equation 7 will be assumed to hold over the whole energy and atomic number range and the expression for the cone apex angle will then be given by

$$\alpha_{\mathrm{c}} = 694\left[\frac{n^{2/3} Z_1 Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{\frac{1}{2}} E}\right]^{\frac{1}{2}} \cdot \qquad (10)$$

The values for α_{c} derived from Equation 10 will be denoted by $(\alpha_{\mathrm{c}})_1$ and are given in Table I for a general cross-section of elements and materials ion bombarded under various conditions. In order to illustrate Z_2/Z_1 dependencies, data for low, medium and high target atomic numbers are given where possible for each ion energy. Table II is restricted to data on gold and is important since a considerable number of experimentally

TABLE I

Target material	Z_2	keV	$(\alpha_c)_M$	(α_{c1})	$(\alpha_c)_2$	$(\alpha_c)_3$	$(\alpha_c)_4$	Ref.
Cu	29	27	24	21	21	18	15	11
Sn†	50	5	20	43	24	20	30	2
NaCl†	14	3.5	13	31	28	24	23	12
Al	13	1.05	39	68	38	33	50	13
Ti	22	1.05	40	120	34	36	86	13
Cu	29	1.05	45	107	47	41.5	76	13
Ag	47	1.05	57	115	49	41	81	13
Ta	73	1.05	50	133	54	43.5	93	13
Fe*	26	0.8	73	215	68	57	133	10
Mo*	42	0.8	81	242	73	58	160	10
W*	74	0.8	85	307	82	64	195	10
Fe	26	0.5	85	148	57	50	106	14
Fe*†	26	0.4	80	305	81	67	207	10
W*	74	0.4	80	434	97	76	276	10
MnS†	19.5	0.3	75	148	62	52	107	1, 15
S. steel†	26	0.3	90	244	57	57	174	1, 16
Ni*	28	0.2	97	457	96	80	305	10
Mo*	42	0.2	100	485	105	81	314	10
W*	74	0.2	94	613	115	90	391	10

All bombarded by Ar (Z_1 = 18) except those marked by * where Hg (Z_1 = 80) was used.

TABLE II

Bombarding ion	Z_1	keV	$(\alpha_c)_M$	$(\alpha_c)_1$	$(\alpha_c)_2$	$(\alpha_c)_3$	$(\alpha_c)_4$	Ref.
Xe†	54	20	40	53	33	26	34	17
			59					17
Ar†	18	20	27.5	32	26	21	22	17
Ar†	18	10	33	45	31	25	32	17
Ar†	18	5	36.5	64	37	30	45	17
Ar	18	1.05	65	140	54	44	98	13

Target material Au (Z_2 = 79)

TABLE III

Bombarding ion	Z_1	keV	$(\alpha_c)_M$	$(\alpha_c)_1$	$(\alpha_c)_2$	$(\alpha_c)_3$	$(\alpha_c)_4$	Ref.
Xe	54	1.05	59	169	59	48	115	13
Kr	36	1.05	49	143	54	47	99	13
Ar	18	1.05	45	107	47	41	76	13
Ne	10	1.05	40	83	41	37	61	13
He	2	1.05	38	39	28	27	30	13

Target material Cu (Z_2 = 29)

measured cone angles are listed. Table III concerns copper subjected to bombardment by a series of different ion species at one given energy, 1.05 keV. The measured cone angles are listed under $(\alpha_c)_M$. Those materials for which the cone angle has been determined by optical or electron microscopy are indicated by the symbol †. For uniformity, all the data due to Wehner [10] has been re-evaluated by putting $S(\theta) = S'(\theta)\cos\theta$ since he deduced a sputtering coefficient $S'(\theta)$ as a function of θ from the rate of erosion of a sphere in a direction parallel to the ion beam and not as generally determined in a direction perpendicular to the target surface. The exception is the case of Fe bombarded by 0.5 keV Ar^+ ions where the sputtering coefficient perpendicular to the sphere surface has been measured directly from a photograph. Data from other materials sputtered by 0.5 keV argon ions has been omitted due to uncertainties caused by insulating particles distorting the final sputtered surface profile. Owing to Wehner's experimental arrangement, his values for angles of incidence can in any event only be considered as nominal.

It is evident from the tabulated values that for incident ions of energy between 20 and 30 keV, the agreement between measured and calculated cone apex angles is fairly presentable. Below 20 keV, however, Equation 10 becomes unacceptable since the calculated values of α_c are always greater than the measured values. The divergence between the two sets of values is seen to increase rapidly with decreasing ion energy and to be greater the smaller the ratio Z_2/Z_1. The latter is particularly noticeable from Table III for copper where the discrepancy is 186% for Xe, 108% for Ne and only 3% for bombardment by He ions.

(2) The second expression for α_c can be obtained by a more rigorous solution of Equation 2. If it is assumed that the incident particle happens to have a lattice atom directly below its orbit at the minimum approach distance, it can be shown that the solution takes the form of

$$\beta^2(1+\beta^2)^2\,[(\beta^2+1)^{\frac{1}{2}}-\beta] > \frac{E_p}{E} \qquad (11)$$

where β is given as $\psi d/Ca$ and d is the atom separation in the lattice. Three conditions are then possible only one of which yields a sensible result. This result takes the form

$$\psi = \frac{Ca}{d}\left[\frac{E_p}{E}\right]^{\frac{1}{4}}. \qquad (12)$$

Substitution of the appropriate values into this equation yields the condition that incident ions of energy E can form a cone on the target surface whose apex angle is given by

$$\alpha_c = \frac{134}{d(Z_1^{2/3}+Z_2^{2/3})^{\frac{1}{2}}} \left[\frac{Z_1 Z_2 (Z_1^{2/3}+Z_2^{2/3})^{3/2}}{n^{2/3}E}\right]^{\frac{1}{4}}. \qquad (13)$$

This expression, in common with Equation 10, is reportedly valid only for more than one collision, that is for ψ less than the total angle of scattering in the laboratory system. It can be seen that the presence of a factor d insures an even stronger structure factor effect than the n found in Equation 10. Such an orientation effect has been observed in sputter yields of various metals, in particular for copper [18, 19]. In theory, at least, it should thus be possible to determine which crystal planes correspond to the faces of pyramid type surface structures that have been observed on some materials [20, 21]. Frequently, such faceting tends to smear out [1, 17].

To obtain a value for α_c, it is necessary to know the correct atom spacing d to fit into Equation 13. This value will be dependent on the initial orientation of the target crystal or grain presented to the ion beam. Experimentally, it appears that there is a correspondence between preferred ejection directions and the expected focusing directions. Atoms are found to be preferentially ejected in the directions of closest packing [4 ,5, 20, 22]. The values taken for d in the present calculations correspond to the atomic spacings in the $\langle 110 \rangle$ directions for fcc structures, $\langle 111 \rangle$ for bcc, $\langle 100 \rangle$ for cubic, $\langle 100 \rangle$ for NaCl type, i.e. $d = a/2$ where a is the lattice parameter, and the basal spacing for hexagonal structures. The value of $\langle 111 \rangle$ for diamond cubic has been averaged and is thus identical to the $\langle 110 \rangle$ spacing. It must be noted, however, that although the most probable atom spacings correspond to nearest neighbour directions in channelling, additional ejection directions are possible for next-nearest and other close neighbour directions. For example, ejections indexed as $\langle 110 \rangle$, $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 114 \rangle$ and $\langle 116 \rangle$ have been reported for fcc metals [23], while for bcc metals $\langle 111 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ ejections have been observed together with emission parallel to the $\{110\}$ planes [22]. If for any reason one or several of these other directions should become important or predominate, the d value would have to be modified accordingly while obvious faceting could disappear.

The cone angle values obtained from Equation 13 are listed under the column headed $(\alpha_c)_2$. The agreement with measured values in all cases can be seen to be very much better than that obtained from Equation 10. An indication of the improvement is that the average deviation of the calculated values of cone angle from those measured is 15% for this formula and 200% from Equation 10. (The latter figure is only meant to indicate a large discrepancy, the actual value being rather meaningless since the deviation is so energy dependent.) Further agreement with measured cone angles could not be achieved by an sensible or systematic adjustment of the integration constant C, although such has been implied by Lindhard [6]. This is not so surprising since the experimental error in the sputter yield data is of the order of the difference between the measured and calculated cone angle.

(3) A further case can be considered from Lindhard's data [24]. This condition is reported to hold only for slow heavy ions in collision with a row of atoms in the form of a string. Using a continuum potential of the form

$$U(r) = \frac{Z_1Z_2e^2}{d}\log\left[\left(\frac{C\,.\,a}{r}\right)^2 + 1\right] \tag{14}$$

reportedly valid for all values of r, it can be shown that by applying both collision time and minimum distance equations, the cone apex angle is given by

$$\alpha_c = \frac{360}{\pi}\left[\frac{Ca}{d\sqrt{2}}\sqrt{\left(\frac{2Z_1Z_2e^2}{Ed}\right)}\right]^{\frac{1}{2}}\cdot \tag{15}$$

Simplified this yields the relationship

$$\alpha_c = 201\left[\frac{Z_1Z_2}{d^3(Z_1^{2/3} + Z_2^{2/3})E}\right]^{\frac{1}{2}}\cdot \tag{16}$$

Note the inverse cube dependence of d, and the absence of n. The values derived from this equation using the d values prescribed in the previous calculation are listed under the column headed $(\alpha_c)_3$. Although the overall average percentage variation between calculated and experimental values is greater than that obtained using Equation 13, being of the order of 22%, the degree of agreement is still good considering the approximations involved. The promise of better agreement for the case of slow heavy ions was not found to materialize in practice.

All the cases of ion bombardment considered here in Tables I to III have occurred under hard-sphere collision conditions. In this regime, the distance of minimum approach is such that the incoming ion does not see the nuclear charge of the target atom since it is screened by orbiting electrons, this being the so-called Screened Coulomb case. The present calculations have been carried out using such a potential. Deviations at lower energies might thus be expected to be in part due to not using a Born-Mayer potential. The Born-Mayer potential is applicable to interactions between ions involving relatively low kinetic energies of the order 0.1 to 10^3 eV. Using this potential, as described below, a value of α_c has been computed for atomic planes in a similar manner to that outlined in case 1.

(4) The potential at a distance z from an atom surface plane is given by Equation 2 where the interatomic potential $V\sqrt{(z^2 + r^2)}$ is replaced by the Born-Mayer potential $A\ \mathrm{e}^{-\sqrt{(z^2+r^2/b)}}$; A is an amplitude factor and b determines the steepness of the potential. In the surface plane, $z = 0$, the smeared planar potential takes the form

$$Y(0) = 2\pi An^{2/3}\int_0^\infty R\mathrm{e}^{-R/b}\,\mathrm{d}R \tag{17}$$

$$= 2\pi An^{2/3}b^2. \tag{18}$$

Applying Equation 4 and assuming as previously that the effective potential $Y(\text{eff}) = Y(0)/2$, it can be shown that

$$\alpha_c = 203\left[\frac{An^{2/3}b^2}{E}\right]^{\frac{1}{2}}\cdot \tag{19}$$

The empirical "combining rule" of interatomic potential of pairs of unlike atoms of atomic number Z_1, Z_2 gives that $A = (A_1A_2)^{\frac{1}{2}}$ and $b = \frac{1}{2}(b_1 + b_2)$. Using the values of the A's and b's tabulated by Abrahamson [25] which are said to be applicable in the range $1.5a_0$ ($\sim$ 1 keV) to $6a_0$ to $8a_0$, the above expression can be easily evaluated. (Note, the b used here is the reciprocal of that employed by Abrahamson.) Cone angles calculated from Equation 19 are listed under the column headed $(\alpha_c)_4$. The calculated values can be seen to be too large diverging from the measured values as E decreases in a similar fashion, but with half the divergence of Equation 10, $(\alpha_c)_1$. The values are greatly inferior to those obtained from Equations 13 and 16. To date no closer agreement has been achieved with measured values using this potential when either the Born-Mayer coefficients due to Abrahamson [25] or Brinkman [26] have been employed.

A few words on sputter yield curves might emphasize the problems involved in cone angle prediction. In the low energy range 0.1 to 1.0 keV it is found that marked deviations occur in the rate at which the sputter yield of different materials rise with increasing ion charge number, energy and mass [27]. The energy dependence of the sputter yield curves is complicated with the result that it is possible for the yield curves of different elements to cross each other once or twice in this region. To date, none of the existing sputter theories that should have been applicable in this region have been able to correctly reproduce all the experimental data. Since sputtering theories have predicted dependences of $E^{\frac{1}{2}}$ to E^2 this might imply that the energy dependence varies with ion energy. Such a possibility has been put forward by Wilson and Kidd [17]. While the angular dependence is known to be complex, it now appears, however, that target materials showing the smallest angular effect are those that give the largest sputtering yields and vice versa [27]. Unlike at higher energies, the angular effect is structure dependent and becomes more pronounced with decreasing atomic number.

3. Summary

The characteristic behaviour of sputter yield curves going through a maximum as the angle of ion incidence is varied appears to result mainly for crystalline materials from the increase in reflection of the primary ion beam at larger angles of incidence. The ion inflection coefficient ρ is known to increase in proportion to Z_2/Z_1 [27]. It is virtually independent of energy, except for alkali ions below about 1 keV when the reflectivity increases rapidly with decreasing energy. In the energy range 0.1 to 1.0 keV, however, no experimental results are available regarding the dependence of ρ on the angle of incidence of the primary beam. Molchanov and Tel'kovskii [11] have observed that the number of 27 keV argon ions reflected at a copper surface increases in the region of the sputter yield maximum. Quantitative corrections to the yield values on the basis of the reflection coefficient by them failed to completely account for the observed behaviour. As explained earlier, contributions from other effects must be expected and these may negate the discrepancy.

From the present calculations, it can be seen that the prediction of cone apex angles is at least in the energy range 0.2 to 27.0 keV best calculated from Equation 13. Since this relationship is based on channelling the importance and predominance of the ion reflection effect is obvious. Further work is currently in progress on ion etching different materials to compare experimentally determined cone angles with the predictions of Equation 13 and correlate the resulting shape changes with theories of topographical development.

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