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Sputter etch profiles of spheres, cylinders and slab-like silica targets

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The intermediate and quasi-equilibrium contours generated by ion bombardment on silica targets under the condition of stationary target and ion beam direction are shown predictable by Frank's construction method. An expression based on ion reflection is reported which yields values for the apex angle of conical silica ion etch structures in agreement with those derived graphically from sputter yield data. The effect of the initial target shape on the etch topography is discussed.

1. Introduction

Considerable effort has been directed towards understanding how the surface contours of materials change when subjected to ion erosion. Both the experimental and theoretical studies have involved metallic and non-metallic, crystalline and amorphous materials. The basic topographical variations on crystalline materials are now reasonably well understood. From a knowledge of the sputter yield curve under the appropriate ion bombardment conditions, Frank's graphical method can trace the erosion surface [1–3]. Calculations based on planar ion channelling have been shown capable of predicting the quasi-equilibrium cone shape apex angles for high [4] and low ion energies [5] in good agreement with both experimental values and those obtained from Frank constructions. On the other hand, the study of amorphous materials has been primarily concerned with glasses, and in particular fused silica, since ion bombardment is a means of shaping optical surfaces. It must be remembered however that ion damage can produce sufficient lattice disorder so as to transform crystalline targets into amorphous materials, so that during an ion erosion process the target can take both crystalline and amorphous states.

The work reported here is concerned with the profile changes produced on amorphous fused silica surfaces eroded by argon ions in the energy range 2 to 32 keV. It makes use of and compares results with the data published by Edwin [6] and Meckel *et al.* [7].

2. Results and discussion

The target, whose initial surface shape is taken to be the solid outer shape in Fig. 1, is a slab extending perpendicular to the paper with a semicircular face directed towards a collimated ion beam which is parallel to the straight sides of the structure. The larger dashed line indicates the cross-section of either a cylinder with long or fibre axis perpendicular to the paper, or a sphere. Both ion source and target are assumed to be in fixed positions.

Edwin [6] has measured the sputter rate of fused silica using argon ions of energy 12 to 32 keV. The slowness of erosion curve shown in Fig. 1 is derived from a construction of the sputter yield curve from eight 16 keV data points. Sputter rates were reported as measured to an accuracy of better than ±10%. The angle of ion incidence to the target surface corresponding to the peak in the sputter yield curve, generally denoted by the symbol $\hat{\theta}$, was equal to about 83°. The orientation trajectories (straight lines) utilized in the Frank construction are shown every 2° in Fig. 1. The derivation of these trajectories together with details of the Frank method will not be described here since that has been covered previously [1–3]. The erosion profiles have been drawn in on the figure at positions down the axis parallel to the ion beam at distances from the front face of 0.05*d*, 0.1*d*, 0.25*d*, 0.5*d* and then by intervals 0.5*d* to 2.5*d* where *d* is the width of the slab (diameter of the cylinder or sphere). It can be seen that the shape of the slowness of erosion curve results in the early loss of the lower angled trajectories. As a consequence, a

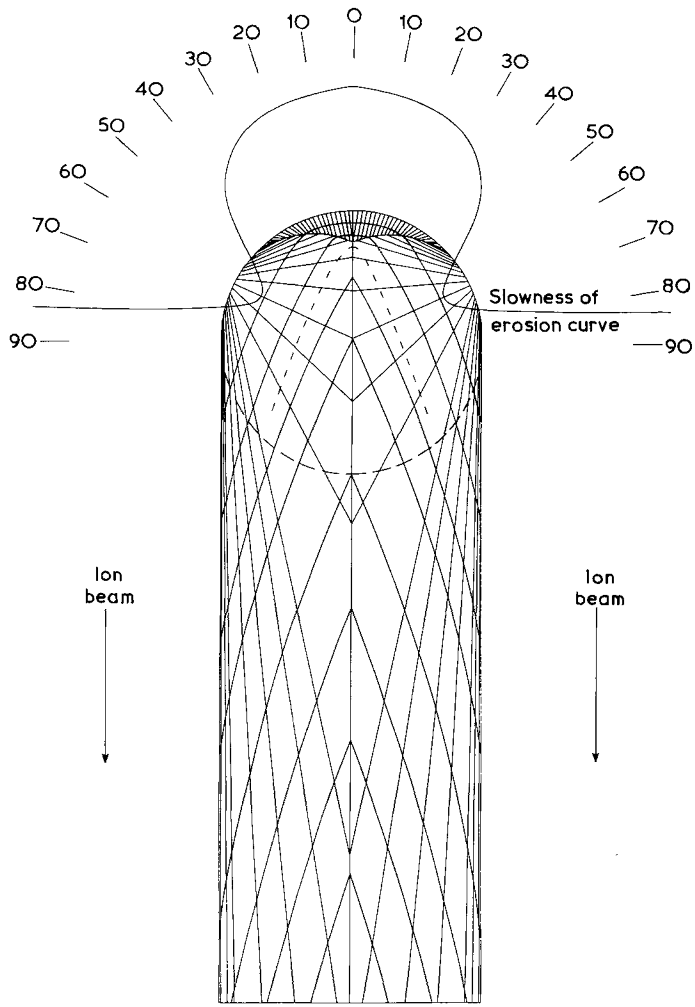

Figure 1 Polar diagram of the slowness of erosion curve, dissolution trajectories and derived profiles of a fused silica slab-like structure etched by 16 keV argon ions.

conical etch profile develops after only about 0.13d of material has been removed in a direction away from the beam. Continued ion bombardment causes the cones sides to become gradually less curved and the apex angle to decrease. The fine dashed lines starting from the 0.135d position correspond to the profile reported by Meckel *et al.* where the ledges at the base of their sputter slopes have been omitted since these appear to be artefacts [7]. A slight asymmetry in the experimental profile can be seen but this probably arises from irregularity in the initial circular cross section (see Fig. 2 of [7]). Similar results have been noted for spherical iron targets [3, 8]. Agreement between experiment and theory is good considering the inherent errors in the approximate sputter yield curve described above.

A quasi-equilibrium sputter etch shape occurs when a cone develops with straight not curved sides. The apex angle α_c of such a profile is given by [4, 5, 9, 10]

$$\alpha_c = 180 - 2\hat{\theta}. \quad (1)$$

In this condition the cone only moves in a direction away from the ion beam, the profile remaining constant until all the material is eroded away. For the present case of silica, Equation 1 yields $\alpha_c \approx 14°$. The speed of approach to this topography is

TABLE I

Axial eroded distance	$(\alpha_c)_F$ at 0.25d	0.5d	1d	1.5d	2d	2.5d
0.25d	57	50	46	42	41	36
0.5d	52	46	44	40	40	35
0.75d	48	44	42	39	38	34
1d	43	41	40	37	36	33
1.25d	40	39	38	35	35	32
1.5d	40	37	36	34	33	30

illustrated in Table I where are listed the averaged cone angle for different amounts of cone apex, measured by cone heights as fractions of d, at different etch positions down the target axis. These measurements are meant to indicate the influence of target shape restrictions on the experimentally determined α_c value. Such shape limitations restrict the number of included orientation trajectories and hence apex angle. It can be seen (Fig. 1) that the fewer included orientation trajectories the larger the cone apex angle. The importance of such restrictions will be discussed later in respect to previously reported experimental results.

The quasi-equilibrium sputter etch profile is achieved when all but the orientation trajectory corresponding to the peak of the sputter yield curve is eliminated from the structure [3]. The axial positions down the slab at which some of the higher angled orientation trajectories are lost are given in Table II. In reality it has been shown previously for crystalline materials that within experimental error the quasi-equilibrium conditions can be considered to have occurred earlier. For the present case this probably corresponds within experimental error to a distance of about $60d$.

TABLE II

Orientation trajectory	Axial position lost
72	$3.3d$
74	$5.1d$
76	$9d$
78	$28d$
80	$65d$

An expression based on planar ion channelling has been derived previously (Equation 10 in [5]) for the cone apex angle assuming that the drop in the sputter yield after the peak at higher angles of ion incidence corresponds to an increase in the ion reflection coefficient. This relationship is given below where the proportionality constant has been altered as a result of a comparision between experimental data on argon ion etching of other amorphous materials and theoretical results. This change is easily accountable in terms of a modified smeared continous planar potential presented to the bombarding ions [11]. The expression for calculating the cone apex angle on amorphous targets is given by

$$(\alpha_c)_A = 590\left[\frac{n^{2/3}Z_1Z_2}{(Z_1^{2/3}+Z_2^{2/3})^{\frac{1}{2}}E}\right]^{\frac{1}{2}} \qquad (2)$$

where n is the number of atoms per unit cell of target material in Angstroms, Z_1 and Z_2 are the atomic numbers of the incident ion and target atom respectively, while E is the ion energy in eV. As expected, Equation 2, unlike the corresponding one for crystalline materials [3–5], is independent of the atom spacing and hence directional effects. The problem remains of determining n since for silica and glasses the limited atom regularity results in an irregular three-dimensional network requiring an averaged number of atoms per unit volume rather than per unit cell. In the calculations for silica, it has been presumed that the target material approximates to amorphized low quartz. The unit cell of low quartz is thus used in the calculations as it is assumed that ion bombardment merely rearranges the atoms rather than causing significant preferential atom type sputtering with resulting compositional change. Although Jorgenson and Wehner [12] have reported preferential oxygen loss for SiO_2 targets in the ion energy range 20 to 120 eV, the more recent high energy work of Kelly and Lam [13] does not show evidence for this. In the present calculations, a value for Z_2 of 10 has been utilized since it has been found to be resonable for SiO_2 previously [14] and because the mass ratio of silicon and oxygen does not exceed two or three [15]. Substitution of the appropriate values in Equation 2 for $E = 16$ keV yields the result $(\alpha_c)_A = 14.1°$, in excellent agreement with that obtained from the sputter yield curve and Equation 1.

It would thus seem that the characteristic surface contours developed on ion etched targets is predictable at all stages of the erosion process given the necessary information such as experimental conditions and some sputter yield data. Indeed this conclusion would now appear true for most types of targets whether crystalline or amorphous [2, 3]. What the Frank method and ion planar calculation cannot at present accommodate are artefacts such as charging which would be expected on dielectrics (insulators) unless appropriate measures were taken to neutralize the charge such as utilizing an electron emitting filament near the surface or electron gun [16]. The small cones seen to occur on target surfaces resulting from inclusions, dust and damaged regions could easily be predicted as long as their shape and sputter yield characteristics are known. It must be stressed that the latter details are frequently not available so that as a rule the appearance of such shapes can be explained but not accurately predicted.

Some comments on recent work are pertinent to the above results. Meckel *et al.* [7] have studied the evolutionary cross-section profiles of silica glass fibres bombarded normal to the fibre axis by Ar^+ ions at energies between 2 and 16 keV. These authors report that the cone apex angle is not related to $\hat{\theta}$ but to an angle called the equilibrium optimum sputtering rate angle (EOSRA) which is smaller than $\hat{\theta}$. Using Equation 1, the cone angles appropriate to these measurements are listed in Table III under the column headed α_c. For comparison are shown the values obtained from substitution of measured $\hat{\theta}$ values in Equation 1 from sputter yield data obtained by Bach [17] for low quartz, a material which becomes disordered by 5.6 keV Ar^+ bombardment, and silica glass and from the data published by Edwin [6] for fused silica. All these results are probably accurate to about ±4°. It can be seen that the results of

TABLE III

keV	α_c	$(\alpha_c)_A$	Reference
2	64	41.3	[7]
3	54	33.8	[7]
5.6	26	24.7	[17]
6	46	23.9	[7]
12	42	16.9	[7]
16	40	14.6	[7]
16	14	14.6	[6]
24	37*	11.9	[7]
24	13	11.9	[6]
32	35*	10.3	[7]
32	12	10.3	[6]

*Extrapolated value.

Meckel *et al.* are in excess of those calculated, the discrepancy increasing with ion energy. In contrast, the data of Bach and Edwin are in good agreement with the calculated cone apex angles. Meckel *et al.* quote their EOSRA values accurate to ±1° so that the error in α_c will be ±2° and cannot account for the variance. Consideration to this apparent discrepancy will be given below.

Meckel *el al.* consider that the EOSRA value determines the cone shape since the $\hat{\theta}$ value pertains to a region in which the ion flux decreases as the cosine of the angle of ion incidence. While it is known that this does occur and in many cases at an even greater rate [18], other factors are of importance. For example, near glancing angle incidence of the ions to the target surface will cause increased ion reflection, the basis of Equation 2, as well as result in the collision cascades being located so close to the surface that backscattering will prevent the cascades from developing fully [19. 20]. Both mechanisms should cause a significant decrease in the sputter yield. Of course, since the collisions are near the surface, the lower energy recoil target atoms will be more able to reach the surface and escape as sputtered atoms and this will work to enhance the yield. While the reflection process would perhaps be expected to be generally less significant during the early stages of ion erosion since surfaces are not normally prepolished, the developing profile changes will tend to smooth the outline and increase the contribution accordingly.

Regarding the characteristic angle of ion incidence corresponding to the cone apex angle, it would seem logical that the surface with maximum sputtering rate will always predominate, this having been shown analytically utilizing the Frank construction [9] and both experimentally [3] and theoretically [4, 5] from cone apex angle measurements. This surface will be at an angle $90° - \hat{\theta}$ to the ion beam, an angle associated with peak sputtering yield. The only effect of ion flux decrease at higher angles is to displace the sputter yield peak to lower angles of ion incidence. It is possible, however, for a target shape to be such that the orientation $\hat{\theta}$ does not fall within the original profile orientation range. Where this occurs the final cone angle is associated with either the highest orientation trajectory present where this is always less than $\hat{\theta}$ or the orientation trajectory present in the last piece of target prior to it all being etched away. In the latter case, the shape of the target regulates the rate of loss of orientation trajectories as can be seen in Fig. 1 by comparing the slab and sphere, and from the values recorded in Table I. In the case of the sphere (Fig. 1) the final cone is related to the orientation trajectory associated with a piece of circumference at 67° to the ion beam. This value presumably directly corresponds to the experimentally determined EOSRA value of 70° quoted by Meckel *et al.* for 16 keV Ar^+ bombardment. This relationship has been tested by constructing Frank diagrams using the sputter yield data of Bach for 5.6 keV ion etching of two quartz samples and Edwin's values for different ion energy sputtering of fused silica. The results are compared in Table IV with those determined by Meckel *et al*; θ_{SF} is the orientation trajectory in the last piece of sphere to be eroded away as determined by the Frank method while θ_{SM} is the EOSRA value obtained on silica glass

TABLE IV

keV	θ_{SF}	θ_{SM}	Reference
5.6	68	66.7	[17]
16	67.5	70	[6]
24	71.5	71.5	[6]
32	73	73	[6]

All silica except 5.6 keV which is average of low quartz $(1 0 \bar{1} 1)$ and quartz glass.

fibres. Agreement is within experimental error. Reliability of profiles from the Frank method applied to silica targets is believed provided by the good agreement between predicted and experimental outlines at 0.135*d* on a silica sphere, see Fig. 10 of [7], and from the results of Barber *et al.* [2]. A cone derived from a sphere as discussed above however is clearly not a quasi-equilibrium shape in the true sense since it is only a result of a limitation on the erosion process provided by the target shape and thus a transitory state. The true quasi-equilibrium shape will only develop at high energies after a great deal of sputtering and probably for most practical cases is never achieved. The low energy range is different and it has been shown that a good approximation to a quasi-equilibrium shape can occur on spherical targets under set conditions. The requirement guidelines are that the target be bombarded by heavy ions such as Hg at energies of say 0.5 keV or less so that typically the value of $\hat{\theta}$ is relatively small, less than 55°, and the ratio of the sputter yields corresponding to the peak and normal incidence, $S(\hat{\theta})/S(0)$, is large. Under these experimental conditions, the early loss of the lower angle trajectories is assured. It is thus clear that if only the final sputter etch conical apex angle is required for a sphere say, this in itself characterising the structure, then the whole Frank construction is unnecessary since all that need be drawn is a circle and sufficient slowness of erosion curve to determine the orientation trajectory which co-intersects the sphere diameter parallel to the ion beam and the back sphere surface.

The power of the Frank continuum kinematic theory of step motion which has been illustrated previously for the chemical dissolution shapes on germanium [1, 21] and lithium fluoride [22], has been extended to ion etch topographies [2] and shown to be effective for crystalline materials such as iron [3] is revealed applicable for amorphous materials by the profiles of ion etched silica due to Meckel *et al.* [7]. For example, under 16 keV bombardment, after 0.12*d* sputter erosion down the diameter parallel to the ion beam of a silica sphere or cylinder cross-section, the experimentally determined averaged cone angle for an axial height of 0.88*d* is measured as about 46°, while that obtained from the present Frank process is 48°. The profile at this stage has been shown to be in good agreement with that predicted, see Fig. 1 here, and Fig. 9 in [7].

While the above examples refer to static target and single collimated ion beams, experimentally determined ion etch profile changes determined under conditions of moving target and/or numbers of ion sources has been studied previously in particular for cylindrical targets [23]. A recent investigation on organic fibres has shown amorphous polymers and undrawn fibres containing some crystallinity such as undrawn polyester and acrylic to develop no surface features. In contrast, drawn semicrystalline fibres were observed always to exhibit ion etch topography in the form of highly oriented features transverse to the fibre axis [24]. The case of a Frank averaged slowness of erosion curve for a rotated crystal has been considered by Barber *et al.* [2].

3. Conclusions

It would appear from this and other work that the characterization of basic ion sputter profiles on amorphous materials in particular under stationary target/ion beam directions is possible. The importance of the initial target shape has been discussed with respect to quasi-equilibrium and the so-called equilibrium sputter etch shape. The prediction of the quasi-equilibrium cone contour at least under argon ion bombardment has been indicated here and in [11] to be reliable. Such a result occurs no matter that the theory is incomplete. Presumably the neglected factors are competing and tend to average out. Further investigation into the subject of amorphous/crystalline material etch profiles is currently being undertaken.

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