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Chemical etching of {1 1 1} and {1 0 0} surfaces of InP

B. TUCK, A. J. BAKER
Department of Electrical and Electronic Engineering, University of Nottingham, Nottingham, UK

The effects of a number of chemical etches on the III-V semiconductor InP were studied, using {100} and {111}-type faces. The (111) and ($\bar{1}\bar{1}\bar{1}$) faces were found to behave differently, and this was attributed to the polarity of the zinc-blende lattice. Curves showing etching rate as a function of penetration were plotted, and it is noted that they demonstrate an enhanced etching rate close to the surface. This is attributed to the damaged surface layer associated with the cutting of a crystal slice. Photographs were taken at various stages of the etching using both the optical and scanning electron microscopes. Both etch pits and etch hillocks were observed. The shapes of the pits are compared to those described in previously published work, and possible reasons for these shapes are discussed. The conditions necessary for the production of an etch hillock are described and it is shown that the measured etching rates are consistent with hillock formation in the case of the 1 HCl:1HNO$_3$ etch. The mechanisms of dissolution are discussed and it is suggested that both activation control of the dissolution process and diffusion control were observed in the work.

1. Introduction

Chemical etching is one of the commonest techniques used in semiconductor work. It is used in device manufacture to produce a shiny damage-free surface in preparation for diffusion procedures etc. It can also be used to study lattice defects, distribution of imperfections and other structural aspects. In particular, dislocations can be studied by the production of dislocation etch pits, using an appropriate etch. This provides a simple method for estimating the density of dislocations in a sample. A good deal of work has been carried out studying the effects of various chemicals both on group IV and group III-V semiconductors. Of the latter, the best investigated material is InSb [e.g. 1-4]. Less work has been carried out on InP, and in this paper the etching rates and surface appearance produced by a number of chemical etches on InP are described.

Two different orientations were used: {1 0 0} and {1 1 1}. InP has the zinc-blende structure. A number of III-V semiconductors having this structure have been shown to demonstrate an interesting polarity about the [1 1 1] direction. {1 1 1} planes in the structure are made up alternately of group III and group V atoms. The planes are bonded alternately by sets of three bonds and sets of a single bond. When the material is sliced along the {1 1 1} planes it is the layers joined by the single bonding that are separated rather than layers joined by triple bonding. This gives rise to one of the two surfaces in a {1 1 1} slice being composed completely of group III atoms. Call this surface (1 1 1). The other surface is made up entirely of group V atoms. Call it ($\bar{1}\bar{1}\bar{1}$). It seems likely that InP also exhibits this polarity, with a {1 1 1} slice having a (1 1 1) surface made up of indium atoms, and a ($\bar{1}\bar{1}\bar{1}$) composed of phosphorus atoms.

Each surface atom is joined to the rest of the lattice by three bonds. The situation is not quite symmetrical, however, for a III-V semiconductor. The group III atom, indium, in this case, has three bonding electrons per atom and the surface indium atoms, therefore, have no "spare" electrons: they are all used up in hanging on to the lattice. The phosphorus atoms, on the other hand, have five valence electrons per atom so that at the surface each atom has two electrons available to take part in a reaction. It might be expected, therefore, that a $(\bar{1}\bar{1}\bar{1})$ surface would be more chemically reactive than a (1 1 1) surface and this proved to be the case with InSb. Because of this polarity, the etching characteristics of the (1 1 1) and $(\bar{1}\bar{1}\bar{1})$ surfaces have to be considered separately.

The {100} surfaces can, in principle, consist either of indium or phosphorus atoms. However, neither is preferred since both types are doubly bonded to the lattice at the surface and real {100} surfaces consist of a mixture of A and B atoms.

2. Experimental procedure

The InP was in the form of single-crystal slices about $\frac{1}{2}$ mm thick. All samples were n-type with carrier densities in the region of 10^{17} cm^{-3}. A preliminary experiment was carried out with the {1 1 1} slices to establish the necessity of treating the indium and phosphorus surfaces separately. A {1 1 1} slice was mounted on a glass slide in black wax so that the slice protruded at right-angles to the slide. It could then be dipped into an etchant so that it was only partly immersed and both {1 1 1} surfaces were attacked at the same time. On removal from the etch, a step could be seen on each side, the depth indicating how much material had been removed. The experiment was tried for each etch and in every case the step-height was different on the two sides. In most cases the difference was quite large and the two surfaces looked different. It was, therefore, necessary to treat the {1 1 1} surfaces separately. A similar set of experiments on {1 0 0} slices indicated no difference in the etching characteristics of the two parallel faces, and the two surfaces were of the same appearance. Therefore, these were not treated separately.

The procedure for the {1 1 1} slices was as follows. A slice about 0.5 cm^2 in area was degreased in acetone, washed in deionized water and then weighed. The sample was mounted on a glass slide by pushing into warm black wax so that only the face to be etched was left exposed. It was immersed in 12 cm^3 of the etchant and agitated for a measured time, usually 2 min. At the end of this time it was removed, washed and immersed in trichloroethylene to remove the wax. The sample was re-weighed and the amount of material removed by the etch calculated. The appearance of the etched surface was observed using both an optical and scanning electron microscope. The sample was then re-mounted in wax and the procedure repeated. New etchant was used at each stage and the total etching time was usually 20 min. It was necessary to remove the wax at each stage because it absorbed a little of the etchant. The slice was turned over and the $(\bar{1}\bar{1}\bar{1})$ face was etched in the same way.

A different sample was used for each etchant and all experiments were carried out at 26°C. This latter precaution was very necessary, since the etches were very temperature-sensitive. The (1 1 1) and $(\bar{1}\bar{1}\bar{1})$ faces were identified by comparing these results with the work of Gatos *et al* [2].

The procedure for {1 0 0} samples was similar, but simpler, as there was no need to mask a surface. The slices were held in the etch using stainless steel tweezers, and agitated. The acidic etches were prepared using 12 N H_2SO_4, HNO_3 and HCl, the dilute HCl being 6 N.

3. Results

3.1. 1 HCl:1HNO$_3$

This etch reacted with the $(\bar{1}\bar{1}\bar{1})$ and (1 0 0) surfaces in a most vigorous way. Small flashes of light followed by minor "explosions" occurred when placing a sample into the etch and removing it. In the case of the (1 0 0) surfaces it happened even while the specimen was immersed. The effect was not observed at all for the (1 1 1) surfaces, however. One possible explanation for this is the following. InP hydrolyses in acid solutions according to the equation [5]

$$InP + 3H_2O \rightarrow In(OH)_3 + PH_3 .$$

If any tetrahydride is formed, PH_4, the phosphine will ignite spontaneously in air to form phosphorus pentoxide [6].

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O.$$

Graphs showing the rate of removal of material as a function of penetration are shown for all three orientations in Fig. 1. They all demonstrate a high initial etching rate: this is presumably owing to the "cutting damage" of the slices, and will be considered later in the paper. The rates then settle down to steady values with the etching rates in the order $(\bar{1}\bar{1}\bar{1}) > (100) > (111)$. The values of the steady rates are shown in Table I. At a penetration of about 200 μm the etching rate on the $(\bar{1}\bar{1}\bar{1})$ surface demonstrates a sharp fall. This probably indicates the formation of a surface film.

On the (1 1 1) and (1 0 0) surfaces, etch pits

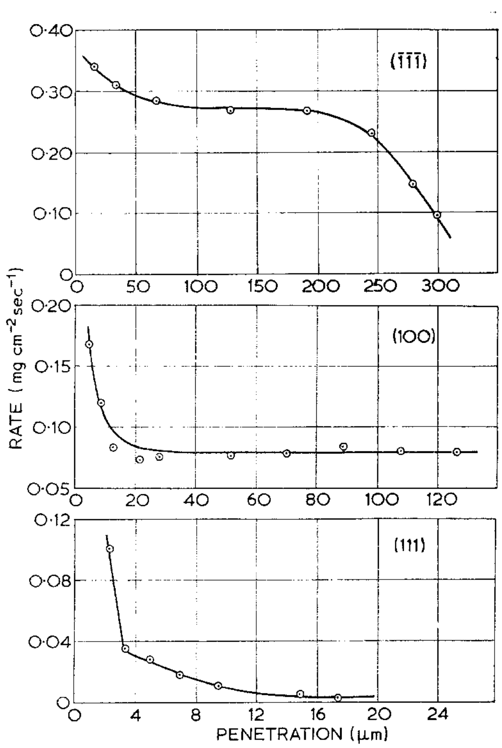

Figure 1 Etch rates versus penetration for etching in 1HCl:1HNO$_3$, at 26°C.

were obtained, triangular and square respectively. An example of the former is shown in Fig. 2. The features of the $(\bar{1}\bar{1}\bar{1})$ surface were quite different. Tetrahedral hillocks developed within the first 2 min of etching: Fig. 3 shows a typical area observed using the scanning electron microscope. The hillocks are of varying size, but all line up exactly. It seems likely that the sides are {100} planes on a {111} base. Hillocks of this type have been observed before on other semiconductors and conditions laid down for their formation [7, 8]. In general, if the various planes of a crystal do not all etch at the same rate it can be shown that the etching of a convex surface will give a polyhedron bounded by faces which exhibit high rates, the corners corresponding to minima in etch rates. Conversely, a concave surface will be bounded by slow etching planes.

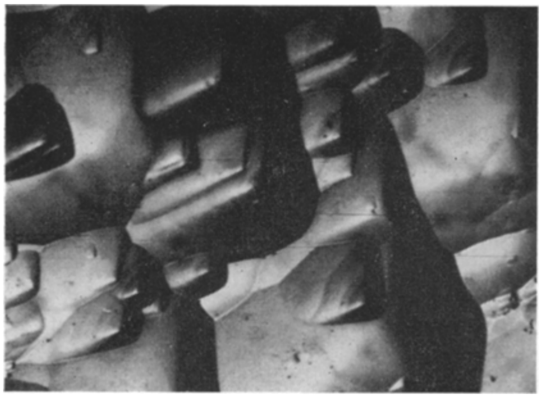

Figure 2 (111) surface etched in 1HCl:1HNO$_3$ for 20 min, showing triangular etch pits (× 170).

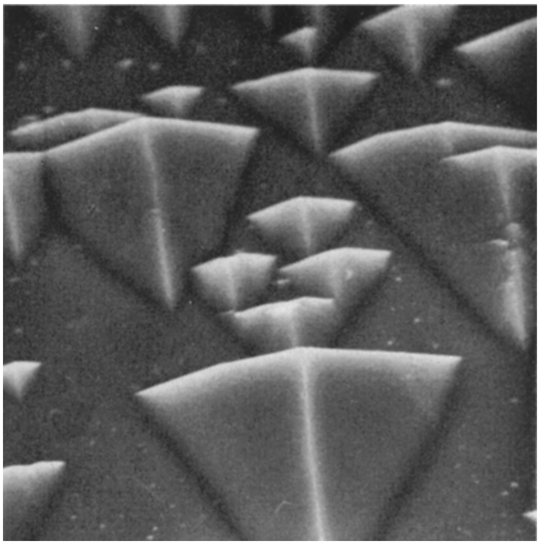

Figure 3 Etch hillocks on $(\bar{1}\bar{1}\bar{1})$, using 1HCl:1HNO$_3$ for 2 min. (× 3200).

Call the etch rate for a hillock plane R_h and that for the surface plane R_g, and let the angle between the planes be θ. The conditions for the stability of a hillock are:

TABLE I

	$(\bar{1}\bar{1}\bar{1})$	(100)	(111)
1. 1HCl:1HNO$_3$	0.27	0.08	0.004
2. conc. HCl	0.15	0.08	0.005
3. 0.4 N Fe^{3+}	0.03	0.03	very small
4. CH$_3$OH:1% Br	0.016	0.03	0.005

Steady etching rates in mg cm^{-2}sec^{-1}.

1. $R_h < R_g \cos\theta$. If this condition is not fulfilled the hillock etches away faster than the ground plane, and disappears.
2. The intersection of two planes in a convex configuration can be stable only if there is no other plane with a higher etching rate lying between them. This may be seen by the following

argument. If the corner of a hillock is considered to be slightly rounded, then it will contain small facets of all the planes lying between adjacent sides of the hillock. If any of these facets have a greater etching rate than the hillock side, then they will grow at the expense of the hillock side and the hillock will change shape. Thus, for a stable shape, the etching rate as a function of orientation must exhibit a minimum at the intersection of the two sides.

It is necessary to have extensive data on the variation of etching rate with orientation in order to predict the form that etch hillocks can take on a given semiconductor. However, the data of Fig. 1 allows us to check Condition 1. Assuming the sides of the hillocks to be $\{100\}$ planes, then $R_h = R_{100}$, $R_g = R_{\bar{1}\bar{1}\bar{1}}$ and $\cos\theta = 1/\sqrt{3}$. Taking the steady-state values of etching rate from the figure, it can be seen that

$$R_{100} < R_{\bar{1}\bar{1}\bar{1}} \cos\theta$$

in agreement with the condition.

After prolonged etching the hillocks disappeared from the surface. This roughly corresponded with the fall in etching rate and possible formation of a surface film.

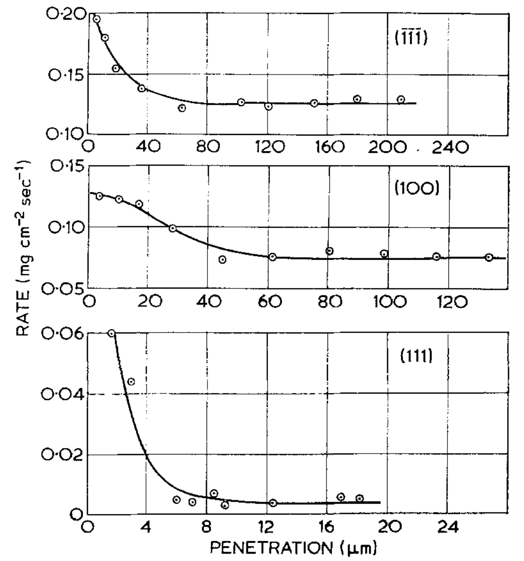

Figure 4 Etch rates versus penetration for etching in conc. HCl at 26°C.

3.2. Concentrated HCl

The graphs showing etching rate against penetration for all three surfaces are shown in Fig. 4. After an initial high rate, all three arrive at a steady rate with $(\bar{1}\bar{1}\bar{1}) > (100) > (111)$. Gas was evolved during etching, being more vigorous from the $(\bar{1}\bar{1}\bar{1})$ and (100) surfaces. The (111) surfaces produced sharply crystallographic features with $\{100\}$ faces revealed, containing small steps, but otherwise quite flat (see Fig. 5). The appearance of the surface did not change significantly between 2 min etching and 20 min.

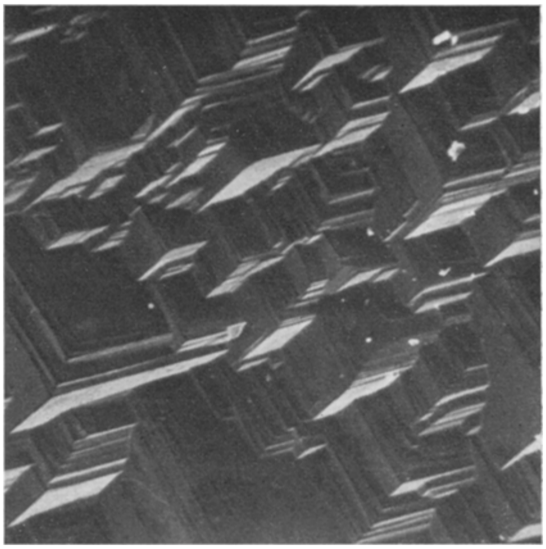

Figure 5 (111) surface etched in conc. HCl for 20 min. (× 300).

The appearance of the $(\bar{1}\bar{1}\bar{1})$ surface did change with time of etching, looking something like Fig. 5 after 2 min. Eventually the rough surface became smoother and tetrahedral hillocks developed on the surface. The orientations of the hillock sides are not known, but they do not appear to be $\{100\}$ as with those developed with the 1HCl:1HNO$_3$ etch. This conclusion is borne out by a consideration of the stability criterion using data from Table I for $R_{\bar{1}\bar{1}\bar{1}}$ and R_{100}. This shows

$$R_{100} \simeq R_{\bar{1}\bar{1}\bar{1}} \cos\theta$$

indicating that a (100)-type tetrahedron would probably be unstable. An interesting background structure to the hillocks was observed. Fig. 6 shows the surface after 20 min etching, giving rise to a herring-bone structure surrounding a hillock. The structure is possibly owing to a large number of hillocks growing into each other.

The (100) surface gave a shiny surface with

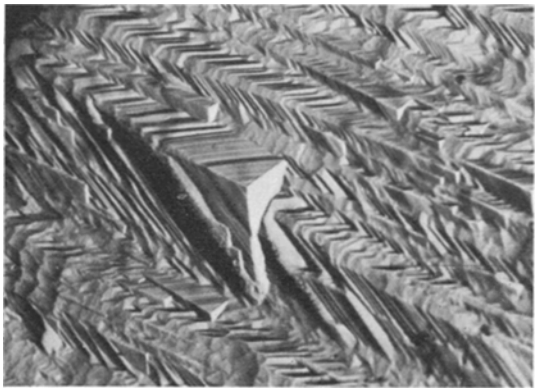

Figure 6 $(\bar{1}\bar{1}\bar{1})$ surface etched in conc. HCl for 20 min. (× 170).

square, pointed etch pits, showing terracing round the sides. A few experiments were carried out using dilute HCl to etch a (100) sample. After removing 0.5 μm, the rate dropped almost to zero. The surface became covered with a film which gave the specimen a matt appearance and also, presumably, caused the low etching rate.

3.3. Fe^{3+} ions in conc. HCl

This etch was prepared by dissolving ferric chloride in hydrochloric acid, so as to make up a 0.4 N solution. The etching rates are shown in Fig. 7 and Table I. The steady rates obtained using this etch were much less than those for the previous two etches. The relationship between the three types of surface was also different with $(\bar{1}\bar{1}\bar{1}) \simeq (100) > (111)$. The $(\bar{1}\bar{1}\bar{1})$ and (111) surfaces both showed triangular etch pits.

The (100) surface demonstrated elongated etch pits, as shown in Fig. 8. These pits are similar to those observed by Gatos and Lavine [1] when etching InSb in a 0.2 N solution of Fe^{3+} in HCl at 82° C. They gave the following explanation for their pits which probably also applies to those observed here. A four-sided etch pit in a (100) surface can have sides of the {111} type. These are (111), $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(1\bar{1}1)$. If all these surfaces etch at an equal rate, then a pit with four-fold symmetry is obtained. Because of the polarity of the zinc-blende lattice, however, one pair of opposite faces will be of group III atoms, and the other pair will be composed of group V. It is clear from Fig. 7 that these pairs of faces will etch at different rates and give rise to an elongated etch pit, as shown in Fig. 9. The elongated pits observed by Gatos and Lavine were flat-bottomed. This was not so with the InP pits: the $(11\bar{1})$ and $(1\bar{1}\bar{1})$ planes met in a ridge at the bottom of a pit.

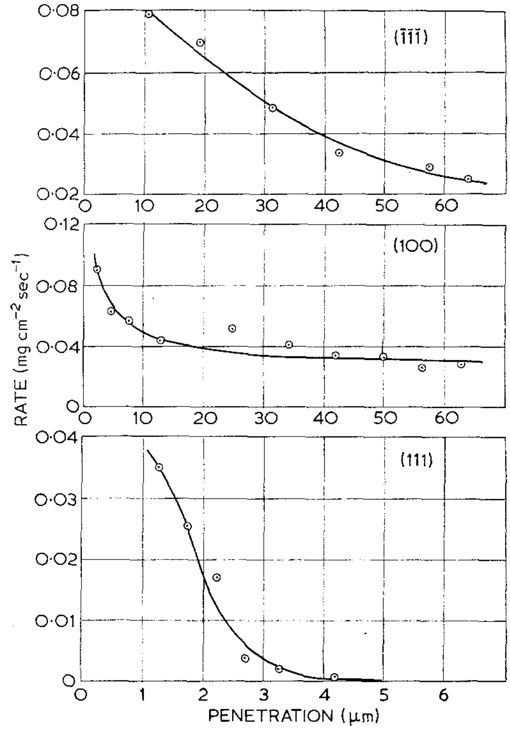

Figure 7 Etch rates versus penetration for etching in 0.4 N Fe^{3+} at 26°C.

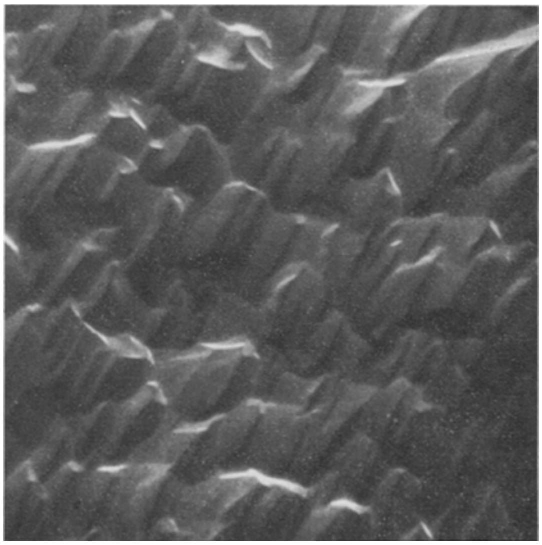

Figure 8 (100) surface etched in 0.4 N Fe^{3+} for 14 min, showing elongated etch pits (× 1200).

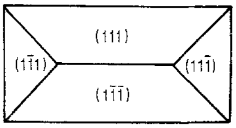

Figure 9 Formation of elongated etch pit on a (100) surface.

A few experiments were carried out using a higher concentration of Fe^{3+} ions. A 4 N solution was made up and used to etch (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces. After removing a few microns, a thick protective film developed on both surfaces and the etching rate reduced almost to zero.

3.4. 1% solution of bromine in methanol [9]

This is an etch commonly used with III-V semiconductors. It was prepared by mixing 10 cm^3 of bromine in 1000 cm^3 of methyl alcohol. The etching rate versus penetration curves, shown in Fig. 10, demonstrate different features to those of the previous etches. The steady etching rates are in a different order, namely (100) > $(\bar{1}\bar{1}\bar{1})$ > (111). The curve for the (100) orientation shows an intitial etching rate which is lower than the steady rate: none of the other etches used showed behaviour of this type. The steady rates were rather low, but they could probably be increased by increasing the proportion of bromine in the solution.

The (111) surface gave a polished appearance and quickly developed rather large hexagonal etch pits. An example is shown in Fig. 11. The pits are similar to those observed by Gatos and Lavine [2] on the (111) surface of InSb after etching with a 0.2 N solution of Fe^{3+} in hydrochloric acid. The form of the pits is quite interesting: they are flat-bottomed and exhibit apparent six-fold symmetry. This second feature must be apparent rather than real, since the zinc-blende lattice does not exceed four-fold symmetry. A similar situation was encountered by Stevenson *et al* [10] when observing symmetrical hexagonal growth whiskers of GaAs. Their explanation or rather the inverse of it since we are here dealing with dissolution rather than growth, may well also account for the hexagonal pits. There are two ways of obtaining hexagonal pits with a (111) base using low index planes; they are shown in Fig 12a and b. Each uses a pair of three-fold axes. In the first, adjacent sides are alternately {110} and {100} and in the second they are {100} and {111}. Neither of these forms gives a symmetrical pit, however, since the edges of adjacent sides are alternately parallel and converging. If both dissolution mechanisms are equally likely, however, both processes will occur and the pit will be the average of the two, showing sides which are alternately {100} and {221}. This gives a symmetrical pit, as shown in Fig. 12c.

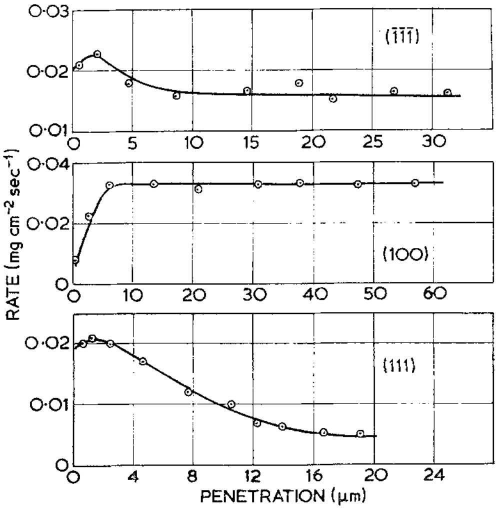

Figure 10 Etch rates versus penetration for etching in CH_3OH:1% Br at 26°C.

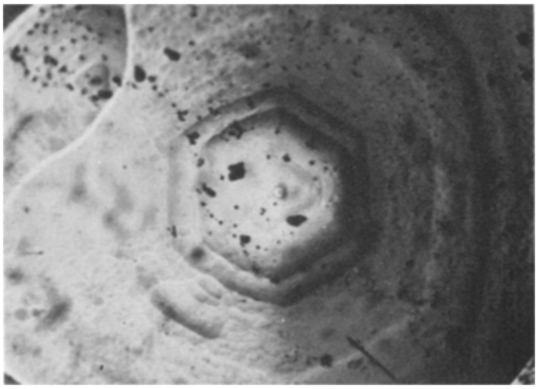

Figure 11 (111) surface etched in CH_3:OH:1% Br for 2 min. (× 160).

The $(\bar{1}\bar{1}\bar{1})$ plane demonstrated a very smooth surface with triangular etch pits. The (100) surface also gave a highly polished, flat surface. Interference photographs of the surfaces showed that any irregularities were less than 0.1 μm. Under high magnification, surface features could be seen on a (100) face. The features resembled flow-lines rather than crystallographic features and probably related to the flow of reaction products over the surface.

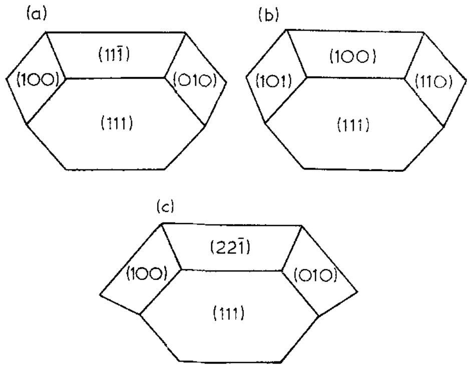

Figure 12 (a) Pit formed from {100} and {111} faces. (b) Pit formed from {100} and {110} faces. (c) Symmetrical pit formed from {100} and {221} faces. Three sides of each pit have been omitted for the sake of clarity. The (111) face is, in each case, the bottom surface of the pit.

3.5. 1 HCl:2H_2SO_4:3HNO_3

This etch was found to be satisfactory only on the (111) surface. The surface had a shiny appearance after being etched and developed a large number of triangular etch pits. Both the ($\bar{1}\bar{1}\bar{1}$) and (100) surfaces developed a grey surface film, however, which slowed the etching rate almost to zero.

4. Depth of damage

In every case except one, the initial rate of etching was greater than the final steady-state value. This effect has been noted before by a number of workers [e.g. 3]. The high rate of etching is due to the damaged nature of the surface which, prior to being etched was in the "as-cut" state, the specimen having been sliced from a single-crystal ingot. An indication of the depth of cutting damage may be obtained from the results by noting the depth below the surface at which the steady-state etching was reached. This data is given in Table II. It is interesting that for the first three etches the results show the same order ($\bar{1}\bar{1}\bar{1}$) > (100) < (111) demonstrated by the steady etching rates. The bromine-methanol etch is relatively insensitive to orientation in this respect. For the first three etches the depths shown for a given orientation are of the same order. It is also worth noting that the variation between the initial high rates is much less than the subsequent differences between the steady rates. This suggests that surface damage has the effect of reducing the differences in etching behaviour between different orientations.

TABLE II

	($\bar{1}\bar{1}\bar{1}$)	(100)	(111)
1. 1HCl:1HNO_3	60	30	15
2. conc. HCl	80	45	12
3. 0.4 N Fe^{3+}	70	30	5
4. CH_3OH:1% Br	10	10	15

Depths of polishing damage in microns.

5. Discussion

When a solid is dissolving in a solution, there are two mechanisms which are likely to determine the rate at which material is removed.

1. The chemical activity of the solid; i.e., the material dissolves as fast as its chemical properties allow and there is no problem concerning the supply of reactants to the surface, or the removal of products from it. Call this activation control. The number of molecules removed in unit time, dn/dt is given by [11]

$$\frac{\mathrm{d}n}{\mathrm{d}t} = kAc \tag{1}$$

where A is the true surface area, allowing for roughness, c is the concentration of reactant at the liquid-solid interface and k is the chemical rate constant.

2. The diffusion of reactants to the surface. The chemical process is so fast that convection and diffusion cannot maintain an appreciable concentration of reactants at the interface. It is usual to assume that there is a layer, effective thickness δ, adjacent to the solid surface, in which reactant is depleted. The rate at which reactant reaches the surface, which is the same as the dissolution rate, can then be determined using Fick's law.

$$\frac{\mathrm{d}n}{\mathrm{d}t} = DA_1\frac{c}{\delta} \tag{2}$$

where D is the diffusion coefficient of reactant in the liquid.

The value to give to A_1 is not obvious. If the surface irregularities are small compared to δ, then A_1 is the projected area of the surface. Since δ is likely to be of the order of tens of microns, this is usually the case. However, it is possible to reduce δ by vigorous stirring of the etching solution: this might happen either by mechanical means or by bubbling occurring as a result of the chemical reaction. In this case, δ might approach the size of the surface irregularities and A_1 would approach A, the true surface area. As long as δ is fairly large and A_1 is the projected area, then Equation 2 suggest that the dissolution should be independent of the nature of the surface. In view of the very large differences found in this work for surfaces of different orientations, it seems probable that the dissolution observed here for the first three etches was activation controlled. The order of polishing rates, namely $(\bar{1}\bar{1}\bar{1}) \geqslant (100) > (111)$ confirms the point made in Section 1 that the $(\bar{1}\bar{1}\bar{1})$ surface would be expected to be more chemically active than the (111). The evidence is not so clear in the case of the bromine-methanol etch, and it is quite likely that diffusion control operated.

It is fairly well established that the enhanced initial etching rate is associated with the layer of cold-working introduced into the slice as a result of cutting or abrading. The depth of crystallographic disturbance has been measured by various techniques, such as X-ray rocking-curve $\frac{1}{2}$-width [12] and found to agree with depth of damage measurements similar to those described in this paper. Good agreement was obtained between the depth of damage results for the first three etches. They gave similar numerical values for the three orientations, with $(\bar{1}\bar{1}\bar{1}) > (100) > (111)$ (see Table II). The bromine-methanol etch gave different results, however, showing similar damage depths for all orientations.

There is some disagreement concerning the detailed mechanism for the extra etching rate in the damaged region. Assuming activation control, then it is possible that the extra rate is owing to an enhanced chemical activity in a region in which elastic strain exists. This amounts to increasing k in Equation 1. On the other hand, it has been suggested that the increased rate of removal might be owing to an increased surface area, A [3]. It seems likely that the true area of an abraded surface is a good deal larger than the projected area. Assuming that the extra rate truly indicates cold-working, however, the explanation seems to require the surface area to be enhanced for the whole depth of the damaged layer; i.e., the degree of strain in the crystal somehow determines the surface area of the sample. There is very little evidence to date that surface flatness is correlated in any precise way with crystal strain, and more work is required to establish whether or not this is a likely mechanism.

The surface-area mechanism might well explain the increased rate for the CH_3OH:Br etch, however. It is possible that the original "as-cut" surface is sufficiently rough to give an increased value of A_1 and hence of diffusion-controlled etching rate. The "depth of damage" measurement will then be the depth at which the surface becomes smooth enough for A_1 to be the projected surface area (which would not necessarily correspond to the depth of cold-working). Under diffusion-controlled conditions this depth would be independent of orientation, as observed.

Acknowledgements

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