THE PREPARATION OF VERY FLAT SURFACES OF SILICON BY ELECTROPOLISHING

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Abstract—Slices of silicon can be very successfully polished by anodic dissolution in a cell using a horizontal rotating disk as cathode, a viscous electrolyte, and a very small anode-cathode spacing (e.g. 150 μ). The surfaces of n-type material of resistivity $>0\cdot05$ Ω-cm must be illuminated during polishing, necessitating perforation of the disk to admit a beam of light to them. The optimum cell voltage is always above that for which the differential conductance of the cell is negative, and is usually about 10 V. The dissolution of 50 μ from a surface initially lapped or mechanically polished leaves it very flat and free of all work damage; electron micrographs show the residual local departures from flatness to be $<0\cdot01$ μ. Material so prepared offers advantages in planar technology and as substrates for epitaxial growth. A full quantitative understanding of the mechanisms involved is still lacking however.

Résumé—Des tranches de silicium peuvent être bien polies par dissolution anodique dans une pile employant un disque de rotation horizontal comme cathode, un électrolyte visqueux et un espace anode-cathode trés petit (par exemple 150 μ). Les surfaces du matériau n-type ayant une résistivité $> 0,05$ Ω-cm peuvent être illuminées durant le polissage, nécessitant la perforation du disque pour y admettre un rayon de lumière. La tension optimum de la pile est toujours au-dessus de celle pour laquelle la conductance différentielle de la pile est négative et est de 10 V habituellement. La dissolution de 50 μ d'une surface initialement recouverte ou polie mécaniquement la laisse très plate et sans dommages; des micrographiques d'électrons démontrent que les écarts résiduels locaux d'applatissement seraient $< 0,01$ μ. Le matériau ainsi préparé offre des avantages dans la technologie planaire et comme couches inférieures dans la croissance épitaxiale. Un traitement quantitatif complet des mécanismes employés manque toutefois.

Zusammenfassung—Gutes Polieren von Siliziumscheiben ist durch einen elektrolytischen Prozess möglich. Man benutzt eine rotierende Scheibe als Kathode, einen viskosen Elektrolyten, und der Anoden-Kathoden-Abstand ist sehr gering (z.B. 150 μ). Die Oberfläche von n-Typ-Material (spez. Widerstand 0,05 Ω-cm) muss beim Polieren beleuchtet werden; man muss also die Scheibe perforieren, so dass ein Lichtstrahl die Oberfläche erreicht. Die optimale Zellspannung liegt immer über derjenigen, für die der differentielle Leitwert der Zelle negativ ist, meist etwa 10 V. Die Auflösung von 50 μ von einer ursprünglich geläppten oder mechanisch polierten Oberfläche ergibt eine völlig flache Fläche ohne Beschädigung. Elektronenmikrogramme ergeben für örtliche Abweichungen von der Flachheit weniger als 0,01 μ. Ein so bearbeitetes Material ist vorteilhaft für technologische Zwecke und dient als Substrat für Epitaxialwachstum. Ein völliges Verständnis des Vorgangs ist noch nicht erzielt worden.

INTRODUCTION

THE etching and polishing of silicon and germanium by chemical action and by electrolysis (anodic dissolution) have been extensively studied and applied to reveal physical imperfections and p-n junctions, to determine crystal orientation and to prepare surfaces for device making.[1] Current needs for extremely flat surfaces, free of all work damage and etch-pits, are, however, inadequately provided for by existing techniques. Thus, although chemical methods provide a near mirror surface if the temperature, concentration and agitation of the etchant are very well controlled,[2] local defects are still present; pits can be seen at sufficient magnification and are found to contain both the products of etching and some solid

particles, which are subsequently difficult to remove. The defects act as nucleation sites when the material is used as a substrate for epitaxial growth, and prevent diffusion processes being carried out with the uniformity required for thin-based diffused transistors, e.g. planar types. Electrolytic polishing in conventional cells also leaves something to be desired; pitting can be very marked on n-type material, and surface irregularities remain with any material.

A recent development[3] uses a cell in which the cathode is a disk rotating in a near-vertical plane and perforated to transmit light to the silicon anode being polished; when the spacing between the cathode and anode is very small and the electrical conditions suitably chosen, excellent polishing is reported. A very brief informal report of earlier work by the same school spurred on our efforts; but considerable differences in techniques have emerged, and are discussed later. Both p-type and n-type silicon of a wide range of resistivity can be polished.

THE APPARATUS

The slices of silicon to be treated are preferably approximately circular and 1–2 cm in dia. and are each lapped or mechanically polished on one face. The reverse sides are nickel-plated and waxed to a circular work-holder (see Fig. 1) of polytetrafluoroethylene (PTFE) or quartz; although not so completely resistant to the electrolyte, quartz is preferred because its use simplifies the waxing of the slices. The work-holder is large enough to take several slices and is suitably drilled to allow electrical connexion to be made to the plating of each slice through the intermediary of some graphite deposited from a coloidal suspension in alcohol. Wires connect the deposited graphite to a single copper bush in the workholder, and a ball-ended copper rod fitting loosely on the bush serves both as the final anode terminal and as a pivot around which the holder can rotate.

The cathode is a rotating disk of much larger diameter (9 in.) machined, integrally with a central shaft, from the solid to minimize distortion during some of the later stages of fabrication. The disk is pierced by closely spaced holes of diameter $\frac{1}{16}$ in. drilled in the annullus of inner diameter 3 in. and outer 8 in. The holes are filled with polystyrene and the upper face of the disk

given a final machining to achieve adequate flatness (in practice, a dial micrometer showed a total variation in height of < 0.002 in. when the disk was rotated in the apparatus). Stainless steel is used as offering the best combination of availability, machinability and resistance to corrosion by the electrolyte.

The disk can be driven smoothly at speeds up to 120 r.p.m. via an infinitely variable gear that facilitates starting and stopping. The electrolyte is a mixture of hydrofluoric acid, water and glycerol which is prepared at room temperature but warms up in use to about $30°C$. It is drip-fed to the centre of the disk and spreads over the surface, in so doing supporting the work-holder on a film of uniform thickness ($0.07–0.30$ mm according to conditions). Low speeds and high glycerol content result in thick films. The difference in velocity of the electrolyte at the inner and outer edges of the work-holder ("inner" and "outer" referring to their positions on the disk) cause the holder to rotate—at speeds of about 20 r.p.m.; the exact value depends, amongst other things, on the rate of supply of the electrolyte. When the electrolyte has spread to the edge of the disk, it is flung off, collected in a surrounding polythene trough, and pumped back to the reservoir mounted above the cathode, for re-use.

Because it has long been established that the anodic dissolution of medium and lightly doped n-type silicon is greatly assisted by a copious supply of holes very close to the surface, an air-cooled 1000-W projector lamp, a condenser and an inclined-plane mirror are fitted to direct a beam of light on to the specimens via the polystyrene-filled holes in the disk. Once it was established that illumination played no part in the polishing of very heavily doped n-type silicon or of any p-type, a solid disk was made and used for these materials.

OPERATING CONDITIONS

The electrical conditions are as important to successful polishing as are the geometry and optics of the cell and the composition of the electrolyte. As the voltage V across the cell is increased, the electrolytic action follows a pattern commonly noted,[1] changing from the formation of a thick amorphous anode film when the current density J is small, through bright etching to gassing and a

heavily pitted surface at high current densities. If at the changeover from thick film formation to bright etching the J/V relationship has a region for which dJ/dV is negative, electropolishing can be expected at slightly higher voltages (see Fig. 2
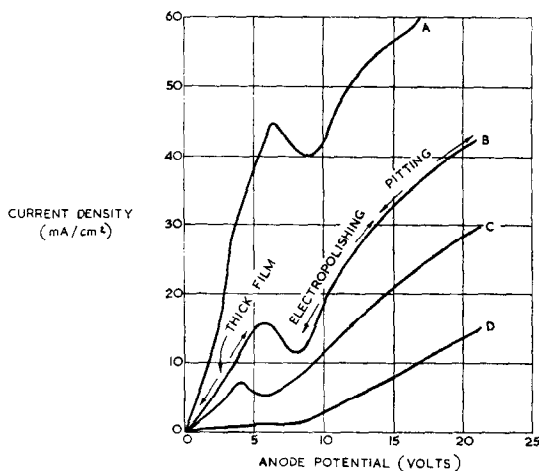

FIG. 2. Effect of HF concentration upon J/V relationships for n-type 1-Ω-cm silicon. The electrolytes contained 200 ml H_2O, 200 ml glycerol and A 10, B 7$\frac{1}{2}$, C 5 ml 40 % HF. Curve D shows a typical dark-current relationship.

for a typical J/V relationship that includes an electropolishing region). The current density J_p appropriate to polishing depends on the following factors: the concentration of HF in the electrolyte, the viscosity of the electrolyte, the speed of rotation of the disk and, for n-type silicon, its conductivity and the level of illumination.

Fig. 2 shows that J_p increases with the concentration of the HF; but polishing may not occur if the concentration is too high (HF/H_2O ratio > 10 per cent). A highly viscous electrolyte results in a low value of J_p (see Fig. 3) as does a low speed of rotation of the cathode; both effects result in part from the influence the two factors have on film thickness as shown in Table 1. That the film thickness does not decrease with increase of speed of rotation in the first row of the table, as it does elsewhere, is because of a tendency for the work-holder to ride on a bow wave for less viscous electrolytes and a high flow rate.

n-type material of such low resistivity that it

needs no illumination and p-type of resistivity < 100 Ω cm both have relatively high values of J_p. n-type material with resistivity greater than about 0·05 Ω-cm requires illumination, the intensity of which helps control J_p; but it is difficult to make a quantitative prediction of the value of J_p expected for a given intensity of illumination, because some of the light that falls on the slice does so in areas
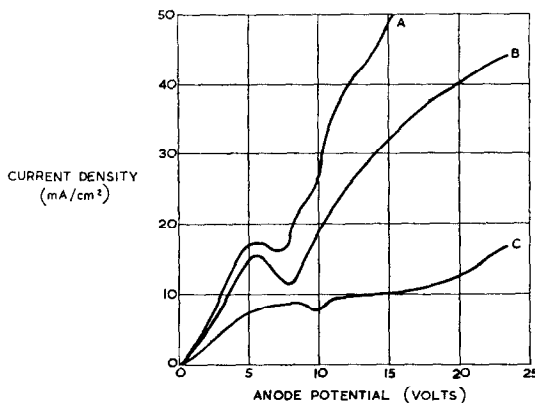

FIG. 3. Effect of H_2O/glycerol ratio upon J/V relationships for n-type 1-Ω-cm silicon. The electrolytes contained 7$\frac{1}{2}$ ml 40% HF and a H_2O/glycerol ratio of A 3:1, B 1:1, C 1:3, in a total volume of 400 ml.

so removed from the cathode that the holes produced may play no part in electrolysis. Consider, for instance, n-type material with a hole lifetime (τ) of 10 μsec, each cathode aperture illuminated having a diameter of 0·16 cm, a mean linear velocity of the cathode disk relative to the slice of 50 cm/sec, and an electrolyte film-thickness of 0·02 cm. Then each area of silicon illuminated moves only 5 μ during a time τ; and the area of material, whose surface layer now has a high hole concentration and has been brought immediately opposite a conducting area of the cathode, is < 10^{-4} cm^2 per aperture. On the other hand, an illuminated area of about 10^{-2} cm^2 (one-half that of an aperture) is always at a distance not greater than 0·03 cm from the cathode and must be considered largely responsible for J_p. Measurement showed that 45 mW of useful radiation (wavelength < 1·1 μ) fell per cm^2 on the silicon surface: of this, something approaching 35 mW enters the silicon and is absorbed with the production of up to 2·2 × 10^{17} hole–electron pairs/cm^2 per

Table 1. *The effect of speed of rotation glycerol concentration and flow rate on film thickness*

Glycerol (%)	Film thickness (mm.) at			Flow rate (ml/min.)
	30 r.p.m.	45 r.p.m.	60 r.p.m.	
33	0·10	0·15	0·18	Continuous 80
	0·10	0·10	0·08	8
50	0·30	0·28	0·23	Continuous 70
	0·20	0·13	0·10	7
75	0·45	0·38	0·35	9
	0·25	0·20	0·18	4

sec. If, therefore, one-half of these holes play a part in electrolysis, J_p should be about 35 mA/cm^2; in fact, a current nearer 20 mA/cm^2 is found. That the longer wave components of the radiation generate holes too far below the surface to play a full part in electrolysis accounts for some part of the discrepancy.

The rate of removal of silicon agrees closely with previous findings, namely 0·47 μ/min for a current density of 25 mA/cm^2 corresponding to an electrovalency of 4; a few measurements on *n*-type material, made with more precision, showed a slightly lower electrovalency, about 3·8, agreeing with the 103–105 per cent current efficiency stated by SULLIVAN *et al.*[3]

RESULTS

All work so far has used slices oriented closely ($\pm 1°$) to the (111) plane. Slices that had first been mechanically polished yielded the most perfect electropolished surfaces when either *n*- or *p*-type material was used, although slices of n^+- and, *p*-type material ground with 5-μ alumina were only marginally inferior. Observations of the finished surfaces by optical microscopy reveal no defects, even though direct viewing of the mirror quality shows very slight waviness over the central area and convexity very close to the edges. The con-

vexity is exaggerated if the nickel plating is applied over the entire reverse face; in practice, the outer 2 mm is kept free of plating.

The departures from flatness over large areas have been measured using an optical flat and simple interferometry; on a slice about 2 cm in dia., the central portion (1 cm dia.) is flat to about 2 sodium fringes (i.e. 0·6 μ) and the portion of diameter 1·6 cm is flat to about 6 fringes (see Fig. 4). Carbon replicas of surfaces were examined by electron microscopy. Typical results are shown in Figs 5 and 6. The local departures from complete flatness have been estimated from both these plates as less than 0·01 μ; the fine structure of Fig. 5 is characteristic of surfaces electropolished from the ground state, becoming more diffused as further material is electrolytically removed, but only slowly even long after all work damage has disappeared. Fig. 7 shows the change in surface structure observed when the cell voltage is increased to 15 V or more; the surface assumes a blue hue, possibly due to the fine structure of the surface having dimensions favouring reflection of the shorter visible wavelengths for some illuminations.

Surfaces have been examined by reflection electron diffraction. Fig. 8 shows a typical pattern obtained when the incident electron beam made a glancing angle of 0° 10′ along a (111) azimuth. Opinion seems divided on the patterns to be expected from surfaces of single crystals neither so smooth as to permit only reflection diffraction nor so coarse as to permit only transmission diffraction, but PASHLEY[4] has submitted that a pattern in which an array of symmetrically elongated spots predominates, indicates a very smooth surface with only small steps or slight rounding of local areas. Kikuchi lines were always present when well-polished surfaces were examined, even though their intensity did not match that of the spot pattern.

In general it has been found necessary to remove a thickness of 50–75 μ from a ground surface to achieve a mirror-like finish. For a mechanically polished surface, the least departure from flatness occurs when a thickness of about 25 μ has been removed—though more must usually be removed to ensure that nothing remains of the region in which the minority-carrier lifetime has been reduced by mechanical working (a total of 40 μ
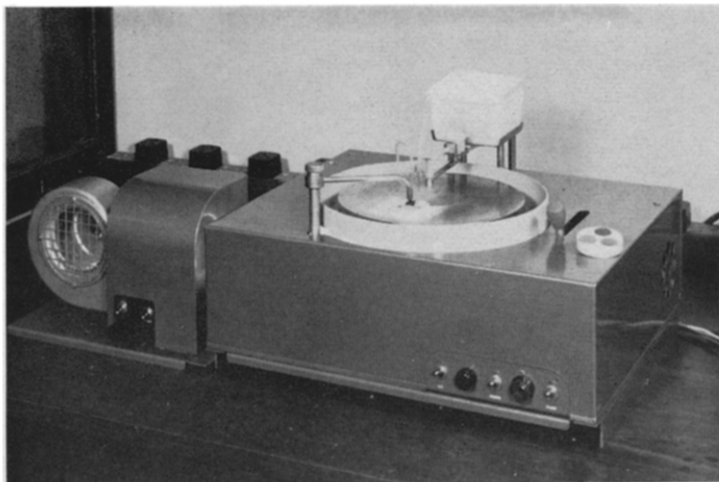
Fig. 1. The electropolishing machine.

Fig. 4. Interferogram of an electropolished silicon surface. A unit fringe separation corresponds to a change in height of 0·3 μ.
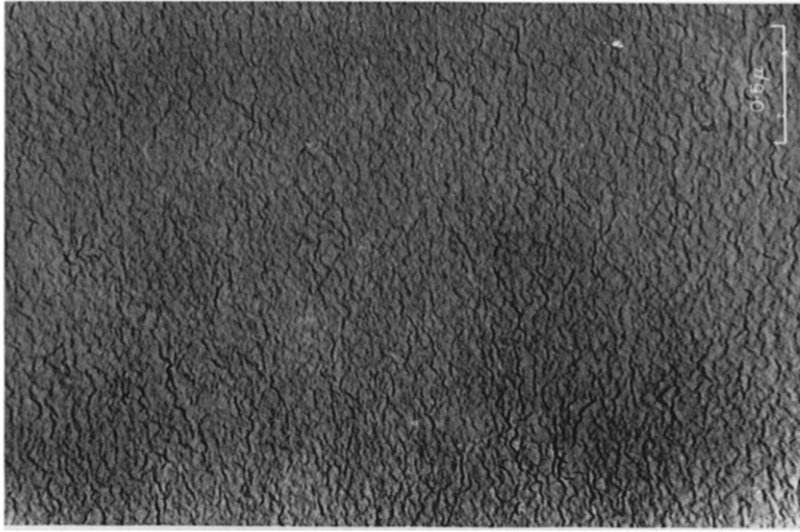
Fig. 6. Carbon replica of n^+-silicon surface electro-polished after polishing with 0.5-μ diamond. Shadowing angle 26°.

Fig. 5. Carbon replica of n^+-silicon surface electro-polished after lapping with 5-μ alumina. Shadowing angle 26°.
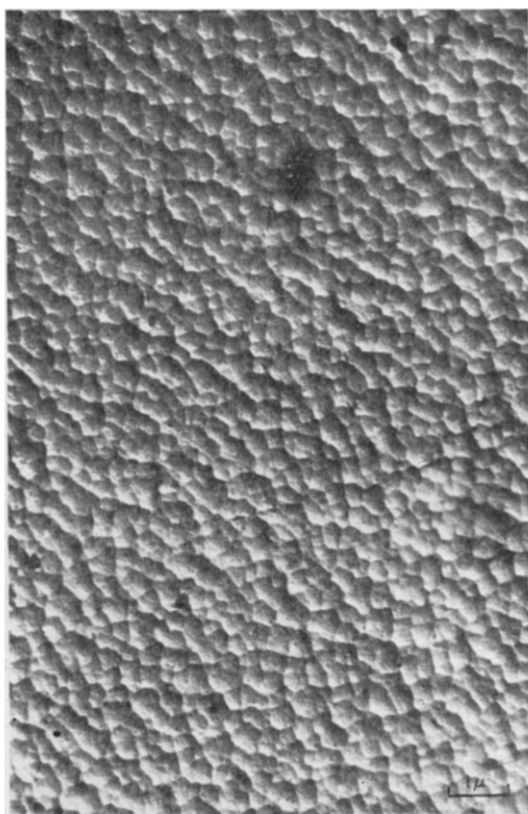
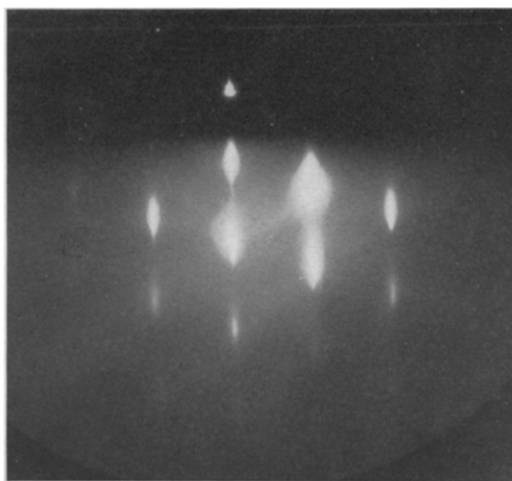Fig. 7. Carbon replica of n^+-silicon surface electro-polished at a high (17 V) cell potential. Shadowing angle 26°.

FIG. 8. Reflection electron diffraction pattern from a
1-Ω-cm n-type electropolished silicon surface.

has been found sufficient when conventional mechanical polishing processes are used and the particle size of the final abrasive is $< 5 \mu$).

The polishing conditions judged best from these observations vary with the starting material, as Table 2 shows; all correspond to a cell voltage of about 10 V.

during polishing in a cell that had anode and cathode well spaced and stationary. His conclusion was that, in the electropolishing region of the J/V relationship, the current density is controlled by the resistance of the oxide film and the rate of arrival of HF at its surface. The present work

*Table 2. Typical polishing conditions at* 10 V *anode potential*

Silicon		Initial surface*	Electrolyte			Current density (mA/cm²)
Type	Resistivity (Ω-cm)		40% HF (ml)	H₂O (ml)	Glycerol (ml)	
p	1	G and P	20	200	200	80
n	1	P	7·5	200	200	20
n	0·1	G and P	7·5	200	300	15
n	0·003	G and P	20	200	200	80

* G = Ground; P = Mechanical polish.

about 10 V. A speed of rotation of 45 r.p.m. is satisfactory throughout. Some heavily doped material has developed grooves or depressions as deep as 1μ when chemically etched or electrolytically polished at high current densities (100 mA/cm²); the irregularities probably indicate variations in doping level. When the current density is reduced below 50 mA/cm², by reducing the HF concentration, they do not form.

DISCUSSION

The mechanisms responsible for electrolytic polishing are not well understood; some of the steps suggested in the electrochemical reactions remain tentative, and little confidence can be placed in any predictions of the J/V relationships. TURNER[5] postulated that SiO_2 is first produced in, effectively, the reaction

$$2H_2O + Si + 4e^+ = SiO_2 + 4H^+$$
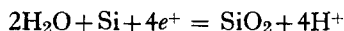
the e^+'s being holes in the valence band of the silicon; the oxide subsequently reacts with HF to form a water-soluble fluoride complex. Thus the generation of four hydrogen ions is predicted for each silicon atom removed from the anode, although TURNER observed little liberation of gas

prompts the following comments on Turner's findings:

(1) Examination by methods that would have revealed surface films of thickness only a few tens of Angstroms has shown no trace of oxide or other solid film, so that no significant fraction of the whole cell voltage can be accounted for by a solid film at the silicon–electrolyte interface.

(2) Gassing has been observed in the present apparatus throughout the polishing region, the more so at the higher current densities used with n^+- and p-material, though it may well all have come from the cathode; additionally, thin dark deposits (possibly containing silicon) have always been found on the cathode in the track of the workholder.

(3) If the rate-limiting process is predominantly that of the transport of HF (or fluoride ions across a thin layer of electrolyte that has been largely exhausted), it might be profitable to make a study of the thickness of the layer and the voltage dropped across it—which surprisingly is as high in the dynamic cell as in TURNER's static cell, if not higher. We return to this thin layer later.

Important though TURNER's work has been, it provides little basis for explaining the much greater flatness obtained with the dynamic cell, where the stirring introduced by the motion of the cathode relative to the anode controls the rate of replenishment of the electrolyte between these closely spaced electrodes and hence any state of exhaustion near the anode. SULLIVAN and his co-workers[3] suggested that the intensive stirring causes the current to be higher at the peaks than in the troughs of the surface of the anode. We have sought quantitative evidence for the suggestion that might, in the extreme, imply that fresh electrolyte is supplied to the high spots while elsewhere the surface is covered with a thin exhausted layer. When, however, a surface was prepared with a few areas, of diameter about 100 μ, projecting 15 μ above the remainder of the surface, very little preferential etching of these areas was noted compared with the general surface; thus the high spots still projected 13 μ after a thickness of 150 μ had been removed. Attempts were then made to prepare a surface with well-defined high spots of much smaller diameter ($< 10 \mu$); little success was achieved and no worthwhile results obtained of preferential etching. More success was achieved with grooves and pits, which are so much more characteristic of ground and polished surfaces than are hillocks.

The grooves were cut and mechanically polished in several slices of silicon and the rate of anodic dissolution in each groove compared with that over the remainder of the polished surface. The grooves were of various initial widths (w_0) and depths (x_0). Fig. 9 shows how the depth (x) of two such grooves—one initially fairly wide and deep and the other narrower and shallow—diminished as dissolution proceeded under conditions for which the anode–cathode spacing was $\sim 150 \mu$. The data are so presented because a simple calculation shows that, if one assumes a near-exhausted electrolyte to cover the surface and groove [see inset (a) of Fig. 9] and the local current density during anodic dissolution to be inversely proportional to the local thickness of this layer, the depth of the groove should vary with the thickness y dissolved from the general surface of the slice, viz:

$$y = (x_0 - x) + h \log \frac{x_0}{x}$$

where h is the thickness of the exhausted layer over the general surface. The broken lines of Fig. 9 show the relationships between x and y for the value of h of 37 μ, where for each line x_0 has been
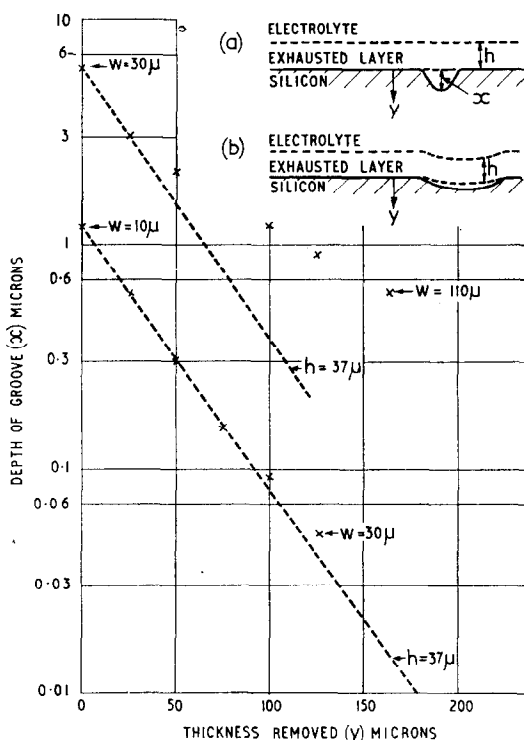

FIG. 9. The variation of groove depth with thickness removed from the general surface.

chosen to bring the line into near-coincidence with the experimental points over some range of y. It will be seen also that each groove has widened as y has increased. The simple model postulated requires $w \leqslant h$ if inset (a) is to apply rather than inset (b), where the upper boundary of the exhausted layer has a contour that tends to follow that of the groove and causes the rate of decrease of x with increase of y to fall, as indeed it does when w exceeds the value of h deduced (37 μ) from the region of the curves for which $w < 40 \mu$. Similar experiments with pits prepared by chemically etching a surface, some small areas of which had been previously mechanically damaged, confirmed a value of h of about 40 μ. These results are therefore consistent with the idea of a thin

exhausted layer being responsible for the preferential etching that yields the extremely flat surfaces, but suggest that the layer is many times thicker than any high spots on the initial surface. The price paid because the exhausted layer is so thick is the need to remove silicon to a depth many times greater than that of the initial irregularities, but it can be afforded because much, at least, of that material needs to be removed to reach damage-free regions.

The decrease of preferential etching for wide grooves and the almost complete lack of it for high spots of diameter of the order of 100 μ may be partly due to the dependence of the local thickness and composition of the exhausted layer on the contours of the surface. If a groove produces etch products that can more than fill the volume of the groove as well as maintain h—by virtue of its real surface area exceeding its projected area—the rate of dissolution at the bottom of the groove will be less than that of the general surface and the groove will disappear fairly quickly. Some simple calculations suggest that this favourable condition is fulfilled for the first two points of the upper set of Fig. 9 and the first three points of the lower set. If the contrary condition applies, i.e. insufficient waste products are formed, inset (b) becomes much more likely with loss of preferential etching. The failure to remove the high spots suggests that the thickness of the exhausted layer above them is not being greatly reduced by any wiping action or other intensive stirring.

The estimate made of the thickness of the exhausted layer is such as to lend support to Turner's view that it is the rate of arrival of HF, which limits the current density; but it is difficult to see how the layer could sustain a voltage drop of ~5 V.

A comparison of the apparatus described by SULLIVAN et al.[3] and that of Fig. 1 shows that most of the differences arise from the change of plane of the cathode. The near-vertical plane eliminates the need to fill the slots or perforations of the cathode with a transparent solid, and is claimed to ease the removal of any gas evolved, though we see no reason for any special means of removal; but, on the other hand, it makes necessary some precise means for maintaining the correct and constant anode–cathode spacing. Very close mechanical tolerances for several parts of the machine might

have sufficed, but the solution adopted was to use a thin transparent separator, e.g. of nylon or paper, between anode and cathode. The separator is attached to the cathode and must withstand the rubbing action of the anode; it must not retain any particles released by the anode, e.g. of abrasive embedded during the previous mechanical working, that could subsequently cause minor damage to the surface of the anode. SULLIVAN et al. did not recirculate his electrolyte, because he feared its contamination by metal ions, which he showed could degrade the polishing of germanium; we have experienced no loss of polishing with recirculation, although fresh electrolyte should be substituted as soon as the loss of the active component causes the current density to fall noticeably (~20 per cent).

A comparison of the results obtained, including the J/V relationships, do not seem to reflect the differences in equipment, practice, semiconductor and electrolyte. Thus the departures from flatness over large areas reported by SULLIVAN et al. for germanium were also about 2 fringes and his electron micrograph of an electrolytically polished surface closely resembles Fig. 6. He measured surface roughness more directly with a Brush Surface Analyser, although "Average Roughness" —the quantity he quotes—may not be a suitable measure of finish for some of the uses to which the surfaces are to be put. He reports also that electrolytically polished surfaces of silicon, of resistivity in the range 0·1–1·0 Ω cm, were rougher, as so measured, than others; if they were not initially well polished mechanically, the result is in accord with our observations.

CONCLUSIONS

The method described of polishing silicon needs only a little care in preparing and mounting specimens—except for some n-type material, that requires previous mechanical polishing—and in maintaining appropriate electrical conditions. It produced surfaces that are superior on a microscopic scale to those previously obtained by chemical or mechanical methods. It will not, however, rapidly improve the flatness of slices with deep scratches, or wide grooves or steps, such as careless lapping or a poorly set cutting machine produces. Because heavily doped material requires no illumination and can dispense with the

nickel-plating on the back face, it can be polished as cheaply electrolytically as it can be mechanically.

Experience with substrate material so prepared indicates that more perfect epitaxial layers grow on it, fewer nucleation centres occurring at the interface; thus, whereas layers grown on some material whose surfaces were prepared by conventional chemical means showed densities of stacking faults of at least $200/cm^2$, those grown on the same material prepared as now described had densities $< 10/cm^2$.

It was also found that when an array of planar junctions was made by diffusing boron into 1-Ω-cm n-type material, the breakdown voltages of the junctions were greater and more constant for surfaces electrolytically polished than for surfaces polished mechanically.

However, despite the practical successes obtained, the subject still lacks a detailed quantitative understanding of the mechanism of polishing and of the roles played by the composition of the electrolyte, the initial state of the surface of the material to be polished and the electrical conditions. While this remains so, modifications, e.g. to handle other semiconductors, will depend largely on experiments, and the full potentialities of the technique may not be realized.

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