

The Anodic Polishing of Germanium

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Slices of p-type germanium, cut parallel to the (111) plane, have been successfully polished by anodic dissolution. The slices were hydrodynamically floated on a viscous electrolyte layer which covered a rapidly rotating cathode. The effect of changing the electrolyte composition and concentration on the current-voltage characteristics and on the final surface finish have been investigated. Under the best conditions, 100 μm of germanium can be removed from the surface, thereby removing all the previous work damage, while retaining the flatness of the surface to better than 1 $\mu\text{m}/\text{cm}$, and leaving a highly polished surface with an average surface roughness of $\pm 100 \text{ \AA}$.

1. Introduction

The preparation of slices of germanium for use in semiconductor-device technology usually involves cutting a slice of the required orientation from a large, single crystal, followed by lapping and mechanical polishing. The mechanical polishing treatment leaves a damaged surface with very high and undesirable recombination rates of excess minority carriers. Measurements of the rate of etching of mechanically polished slices have shown [1] that the depth of damage for germanium is approximately the same as the particle size of the abrasive. Dissolving the work-damaged layer in a chemical etch restores the electrical properties of the surface, but it does not, in general, retain the surface flatness or the optical finish.

Electropolishing of germanium slices with a rotating cathode and a small anode-cathode separation seems to offer the best prospects of removing the work-damaged layer while retaining the surface flatness and optical finish. Studies of the electropolishing of germanium have been carried out by Sullivan *et al* [2] and Bogenschütz [3], using dilute solutions of potassium hydroxide (0.01%, 0.1%) and glycerol as the electrolyte. A thin sheet of cloth or paper covered the cathode to ensure that the anode and cathode had no direct contact. In the present work an apparatus using a rotating horizontal cathode, developed in these laboratories for electropolishing silicon [4], has been used with the

germanium slices floating on a layer of electrolyte. A range of electrolyte solutions and concentrations has been studied.

In most electropolishing systems, the current density at first increases as the voltage is raised, then becomes constant over a considerable voltage range, and finally increases again. It is in the region of constant current with increasing voltage that polishing action is usually found [5]. A plateau in the current-voltage curve is expected whenever diffusion, of a species involved in the reactions taking place at the electrode, is a controlling factor. Diffusion control may arise in a number of ways. The solution adjacent to the electrode may become saturated with reaction products, which must diffuse into the bulk of the solution, or the concentration of a reactant may be reduced at the surface of the electrode, so that the rate of the electrochemical reaction will depend upon the supply of reactant from the bulk of the solution. Diffusional limitation of the rate of reaction may be assisted by the formation of a solid film of products on the electrode surface, through which ions have to diffuse in order to support the electrochemical reaction.

Elmore [6] considered that the plateau in the current-voltage curve arose from the saturation of the solution adjacent to the anode with products of the anodic reaction. This hypothesis of Elmore's did not explain a number of experimental observations, and Edwards [7] suggested

that the current plateau is due to limiting diffusion of "acceptors" for metal ions, moving to the anode. He concluded that the mode of smoothing in electropolishing results solely from variations in concentration gradient within the diffusion layer. The limiting value of the current density corresponds to a maximum concentration gradient, when all the "acceptors" reaching the anode surface react immediately with the surface or with metal ions from the surface.

Wagner [8] made a mathematical analysis of an ideal electropolishing system based on the mechanism suggested by Edwards. He assumed that the anode surface topography consisted of undulations whose amplitude was less than their wavelength, and that the wavelength of the undulations was less than the thickness of the diffusion layer. The rate of smoothing calculated on this basis is in good agreement with the experimental results of Edwards. Wagner's theory also shows that the microroughness of the surface shall disappear faster than the macro-roughness; this is in keeping with our experimental observations and with those of previous workers, since anodically polished surfaces give a specular reflection before the long-wavelength undulations have been removed.

2. Experimental

2.1. Apparatus

In most of the previous work [2, 3, 9] on the electropolishing of germanium and silicon, an apparatus similar to that first suggested by Sullivan *et al* [2] has been used, consisting of a nearly vertical, circular plate which acted as the cathode and was rotated at speeds up to 100 rev/min. An electrolyte was dripped onto the cathode, which was covered with a thin sheet of cloth or paper in order to prevent direct contact between the cathode and the germanium anode. With one exception [4], later workers also used a cloth or paper spacer between the anode and cathode.

In the present investigation, a modification of Sullivan's technique has been used. The apparatus is shown in fig. 1. The technique differs from Sullivan's in that no spacer is required. The slices of germanium are mounted on a quartz disk. The cathode is a horizontal, stainless-steel disk which can be rotated at speeds up to 120 rev/min. A controlled flow of electrolyte from a reservoir is directed to the cathode, and, if the quartz holder and the germanium slices themselves are carefully aligned, the whole



Figure 1 The electropolishing machine.

anode assembly floats on the electrolyte. A metal rod fits loosely into a central metal cup on the quartz-specimen disk and locates the germanium slices in a fixed position with relation to the rotating cathode. The rotation of the cathode produces a differential drag across the specimen disk, causing it to rotate about the loosely pivoted locating rod, which also acts as an electrical contact to the germanium slices through a conducting liquid placed in the metal cup.

Thin slices (approximately 1 mm) of germanium were sawn parallel to the (111) plane from a single crystal of p-type germanium of about 1 ohm cm resistivity. After being degreased, the slices were electroplated on one side with nickel, to provide an ohmic contact. It was found that a more uniform and adherent layer of nickel was obtained if a thin deposit of nickel was first applied from an electroless nickel plating solution. Wires were soldered to the electroplated nickel layer, and the germanium slices were mounted on to the quartz plate with wax. The wires from the back of the germanium slices were led through holes in the specimen disk and made electrical contact to the metal rod, through the conducting liquid.

Three slices of germanium, each approximately 3 cm² in area, could be mounted on the specimen disk. The mounted slices were then lapped flat and mutually coplanar with 11 μ m emery powder, because satisfactory flotation of the germanium slices and rotation of the specimen disk were sensitive to the overall flatness of the

composite anode assembly. A final polish with 1 μm diamond paste on a cloth-covered polishing wheel was given to the mounted germanium slices before polishing anodically.

The usual working procedure is to start the electrolyte flowing onto the stationary cathode at the desired rate. When electrolyte covers the cathode, the specimen holder is placed in position. The metal pivot is then lowered into the metal cup on the specimen holder, allowing a sufficient gap for its floating action when the cathode is set in motion at the required speed. Current is then switched on from a source of constant voltage.

The electrical characteristics of the cell were determined by altering the voltage across the anode and cathode and observing the current, allowing an interval of about 5 min for the current to become constant. The current density and the cell resistance were computed from a knowledge of the surface area of the germanium and the above data. The edges of the germanium slices were protected with wax so that only the faces were in contact with the electrolyte. The standard electrolyte was a 1:1 mixture of a dilute potassium hydroxide solution and glycerol. The cell voltages used for electropolishing the germanium were chosen, after the current-voltage characteristics had been measured for a given solution, to ensure that the anodic dissolution occurred on the plateau portion of the curve. The standard rate of flow of electrolyte was 100 ml/min, and the usual speed of rotation of the cathode was 90 rev/min.

3. Results and Discussion

3.1. Electrical Characteristics

A number of detailed investigations [5] of the electropolishing of metals have shown that electropolishing occurs in the region where the current is constant with increasing applied voltage. In the present work, the same general behaviour has been found.

In fig. 2, the typical variation of current density with the applied cell voltage is shown for different concentrations of potassium hydroxide in the electrolyte. In the first region, where the current density increases rapidly with applied voltage, no appreciable polishing occurred. At an applied voltage of approximately 2 V, with concentrations of potassium hydroxide in excess of 0.1%, an inflection in the current-voltage curve was found. This inflection became more pronounced with greater concentrations of

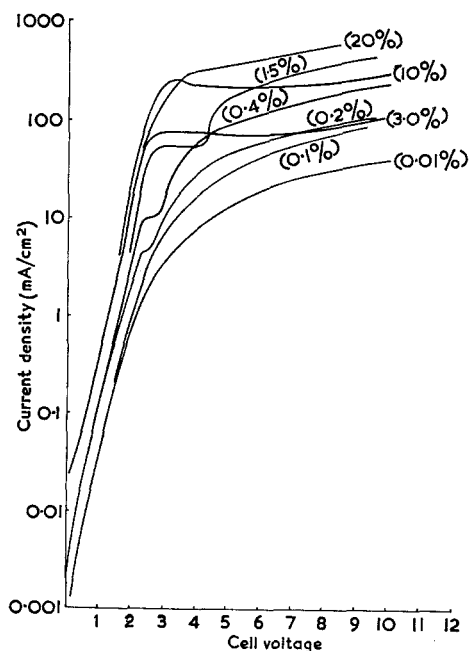


Figure 2 The current-voltage relationship for various concentrations of potassium hydroxide in the electrolyte.

potassium hydroxide, and eventually became a plateau extending over many volts. Polishing of the germanium slice occurred in this plateau region. Further increase in applied voltage at the end of the plateau led to an increase in the current and caused pits to form on the slice. The increase in current for a given voltage increase was larger the smaller the concentration of potassium hydroxide.

Sullivan *et al* [2] reported that the best electropolishing occurs in the current-voltage region where there is a general constancy of the cell resistance with increasing applied voltage. This criterion was probably used because a clearly defined plateau in the current-voltage curve was not observed with the very dilute solutions of potassium hydroxide used. Curves of resistance against applied voltage are shown in fig. 3 for various concentrations of potassium hydroxide solution. With low concentrations ($< 0.2\%$), there is a general levelling of the resistance-voltage curve at the higher applied voltages. At greater concentrations, a step appears in the curve, corresponding to the plateau shown in fig. 2. However, it is interesting to note that the best electropolishing is obtained, according to Sullivan [2], with an applied voltage in excess of 2 V, and that in our work with more concentrated solutions of potassium hydroxide this

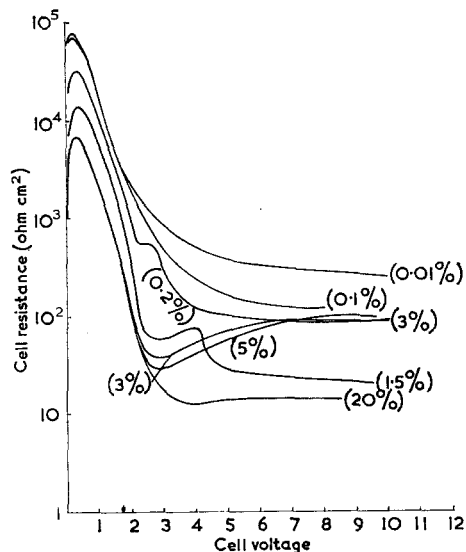


Figure 3 Change of cell resistance with applied voltage for various concentrations of potassium hydroxide in the electrolyte.

voltage corresponds to the start of the current plateau.

The work described here was confined to p-type germanium in order to avoid having to make provision for the photo-injection of positive holes. It is now well established that the anodic reaction consumes positive holes rather than generates electrons, leading to minority carrier depletion and concentration polarisation in n-type anodes at currents well below the electropolishing region. However, there is no reason to doubt that the polishing conditions recommended here would apply also to suitably illuminated n-type germanium.

3.2. Electrolyte Composition

It has been suggested that the role of glycerol in the electrolyte mixture is to increase the viscosity and therefore increase the thickness of the diffusion layer at the anode. The control of viscosity is particularly important in the present work, because the hydrodynamic behaviour of the system critically depends on viscosity: the distance between the floating germanium slice and the cathode increases with increase in viscosity. A number of polyhydric alcohols have been substituted for glycerol in order to test whether the role of glycerol is simply to increase the viscosity. Trimethyleneglycol, ethylene glycol and a mixture of trimethyleneglycol and man-

nitol were examined in turn, and the current-voltage characteristics of the cell were determined. The concentrations of the above alcohols were adjusted in order to ensure the same bulk viscosity as with the standard glycerol solutions. The current-voltage curves obtained with all these alcohols were similar to those found with the electrolyte containing glycerol and a current plateau was observed with each solution. However, none of these solutions caused electropolishing. The solutions containing trimethyleneglycol left a thick film on the surface of the germanium: removal of this film revealed a matt germanium surface. With ethylene glycol solutions, there was no visible surface film after an attempt to electropolish, but again the germanium surface had a matt finish.

Thus, it appears that successful polishing depends not only on having a viscous medium and a plateau in the current-voltage curve, but also on the specific nature of the alcohol. The overall reaction for anodic dissolution of germanium in alkaline solution may be written as follows:



Mannitol forms complexes with mono-germanic acid more strongly than glycerol does; ethylene glycol forms complexes extremely weakly [10]. This suggests that the complexing behaviour of the alcohol, which is added to the electrolyte mixture primarily to increase the viscosity, is of importance in the production of electropolished germanium surfaces. It is not clear, however, why the effect of complexing action in the electropolishing is not monotonic.

A slice of germanium electropolished in dilute solutions of potassium hydroxide containing glycerol sometimes has a misted appearance if the slice is left in the electrolyte solution after the current is switched off, or if the rate of flow of electrolyte and the speed of rotation of the cathode are both small. Under microscopic examination, the misted surface appears to be covered by a surface film. The usual electropolished surface finish can be restored by gently rubbing the surface with a cloth moistened with a 10% solution of sodium hypochlorite. With more concentrated solutions of electrolyte, the misting did not occur under any conditions of rate of flow of electrolyte or speed of rotation of the cathode.

3.3. Surface Characteristics

The surface of a slice of germanium viewed under high magnification after mechanical polishing appears to consist of peaks and valleys with a number of nearly straight grooves. This surface was flat to $1 \mu\text{m}/\text{cm}$ and the roughness was about $\pm 0.1 \mu\text{m}$.

There is some conflict as to the extent of work damage remaining after mechanical polishing. The experimental investigations of surface damage in semiconductors, reviewed by Buck [1], indicate that the depth of damage from mechanically polishing germanium is approximately the same as the size of the abrasive particles. However, it has been reported [11] that the depth of damaged material (assessed by measurements of the surface recombination

velocity of excess minority carriers) can be as large as 36 to $60 \mu\text{m}$ for abrasive particles of 0.5 and $25 \mu\text{m}$ diameter respectively. More recent etching studies [12] have confirmed that the depth of damage produced by polishing with $5 \mu\text{m}$ alumina is $40 \mu\text{m}$.

The progress in polishing a slice of germanium, from the stage of sawing from a single crystal to the final electropolished finish, is demonstrated by fig. 4, which shows Talysurf records of the surface at various stages of polishing using a stylus $2.5 \mu\text{m}$ in diameter. It should be noted that, with a Talysurf stylus of this diameter, any scratches or pits with a surface dimension less than $2.5 \mu\text{m}$ will only appear as small indentations on the Talysurf record, and their true depth will not be revealed. With the surface

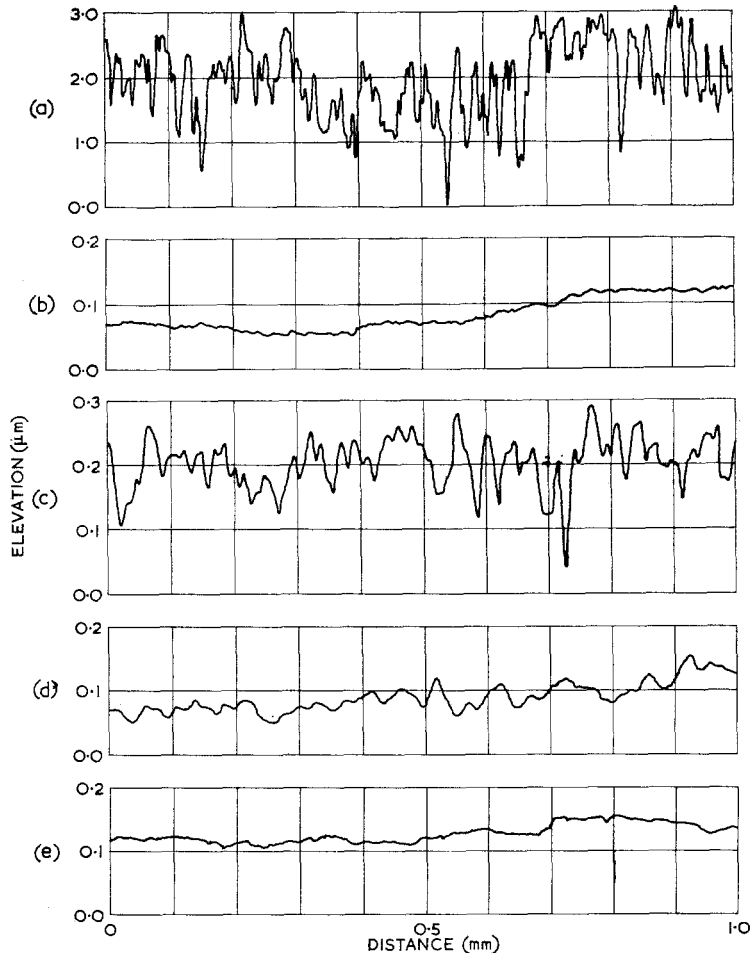


Figure 4 Talysurf traces of several germanium surfaces: (a) after sawing; (b) after mechanically polishing with $1 \mu\text{m}$ diamond paste; (c) after removing $25 \mu\text{m}$ by electropolishing; (d) after removing $50 \mu\text{m}$ by electropolishing; (e) after removing $100 \mu\text{m}$ by electropolishing.

polished with 1 μm diamond paste, a microscope photograph gives a more critical assessment of the surface than the Talysurf record. After electropolishing for 15 min, and removing approximately 25 μm , the surface roughness had increased but the scratches had been removed. The surface at this stage, when viewed under high magnification, appeared highly pitted and rough. Further electropolishing (which removed 50 and 100 μm) resulted in the surface becoming smoother; the pits decreased in number, became progressively more shallow and finally were only slight undulations. This behaviour was also found with solutions containing different concentrations of potassium hydroxide; it appeared that, in order to remove the undulations which developed in the first few minutes of "electropolishing", a total of 70 μm had to be removed by further anodic dissolution.

This initial roughening of the surface with electropolishing appears to be related to the depth and extent of the work damage left by the mechanical polishing. It has been suggested [1] that the surface damage consists of two parts: a thin layer at the surface of highly fragmented material or possibly microcracks, and a deeper layer of plastically deformed germanium. Thus, the initial roughening may be due to the widening of the microcracks on anodic dissolution of the germanium and the relatively faster dissolution of the plastically deformed areas. Once sufficient material has been dissolved to remove the damaged surface layers, the surface becomes progressively smoother with further anodic dissolution, and the electropolishing action becomes evident. A typical electron micrograph of the final electropolished surface is shown in fig. 5. A surface replica technique was used with a shadowing angle of 26° . The slight undulations with a width of about 100 \AA were always found on the surfaces which had been electropolished by this technique. Further electropolishing was not found to improve this level of surface perfection.

4. Conclusions

A current plateau, becoming more pronounced at higher concentrations of electrolyte, has been observed in the electrical characteristics of a cell, consisting of a germanium anode separated by a thin electrolyte layer from a rotating cathode. Successful anodic polishing of germanium was carried out in the plateau region. Substituting a number of polyhydric alcohols for glycerol in

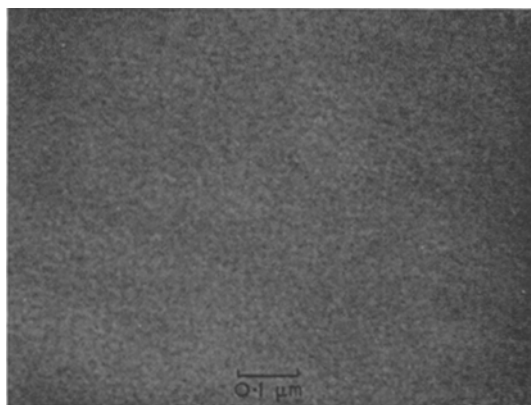


Figure 5 A carbon replica of a typical germanium surface after dissolving 100 μm by electropolishing. Shadowing angle was 26° .

the electrolyte has not led to a suitable alternative solution for electropolishing germanium. Studies of the surface topography with increasing periods of electropolishing showed an initial increase in the surface roughness, but, after sufficient germanium had been removed (100 μm), the surface roughness was reduced to about $\pm 100 \text{\AA}$ and the deviation from flatness of the surface was less than 1 μm .

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