Electrolytic Shaping of Germanium and Silicon

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Properties of electrolyte-semiconductor barriers are described, with emphasis on germanium. The use of these barriers in localizing electrolytic etching is discussed. Other localization techniques are mentioned. Electrolytes for etching germanium and silicon are given.

INTRODUCTION

Mechanical shaping techniques, such as abrasive cutting, leave the surface of a semiconductor in a damaged condition which adversely affects the electrical properties of p-n junctions in or near the damaged material. Such damaged material may be removed by electrolytic etching. Alternatively, all of the shaping may be done electrolytically, so that no damaged material is produced. Electrolytic shaping is particularly well suited to making devices with small dimensions.

A discussion of electrolytic etching can conveniently be divided into two topics — the choice of electrolyte and the method of localizing the etching action to produce a desired shape. It is usually possible to find an electrolyte in which the rate at which material is removed is accurately proportional to the current. For semiconductors, just as for metals, the choice of electrolyte is a specific problem for each material; satisfactory electrolytes for germanium and silicon will be described.

The principles of localization are the same, whatever the electrolyte used. Electrolytic etching takes place where current flows from the semiconductor to the electrolyte. Current flow may be concentrated at certain areas of the semiconductor-electrolyte interface by controlling the flow of current in the electrolyte or in the semiconductor.

LOCALIZATION IN ELECTROLYTE

Localization techniques involving the electrolytic current are applicable to both metals and semiconductors. In some of these techniques,

the localization is so effective that the barrier effects found with n-type semiconductors can be ignored; if not, the barrier can be overcome by light or heat, as will be described below.

If part of the work is coated with an insulating varnish, electrolytic etching will take place only on the uncoated surfaces. This technique, often called "masking," has the limitation that the etching undercuts the masking if any considerable amount of material is removed. The same limitation applies to photoengraving, in which the insulating coating is formed by the action of light.

The cathode of the electrolytic cell may be limited in size and placed close to the work (which is the anode). Then the etching rate will be greatest at parts of the work that are nearest the cathode. Various shapes can be produced by moving the cathode with respect to the work, or by using a shaped cathode. For example, a cathode in the form of a wire has been used to slice germanium.[1]

Instead of a true metallic cathode, a "virtual cathode" may be used to localize electrolysis.[2] In this technique, the anode and true cathode are separated from each other by a nonconducting partition, except for a small opening in the partition. As far as localization of current to the anode is concerned, the small opening acts like a cathode of equal size and so is called a virtual cathode. The nonconducting partition may include a glass tube drawn down to a tip as small as one micron diameter but nevertheless open to the flow of electrolytic current. With such a tip as a virtual cathode, micromachining can be conducted on a scale comparable to the wavelength of visible light. A general advantage of the virtual cathode technique is that the cathode reaction (usually hydrogen evolution) does not interfere with the localizing action nor with observation of the process.

In the jet-etching technique, a jet of electrolyte impinges on the work.[3, 4] The free streamlines that bound the flowing electrolyte are governed primarily by momentum and energy considerations. In turn, the shape of the electrolyte stream determines the localization of etching. A stream of electrolyte guided by wires has been used to etch semiconductor devices.[5] Surface tension has an important influence on the free streamlines in this case.

PROPERTIES OF ELECTROLYTE-SEMICONDUCTOR BARRIERS

The most distinctive feature of electrolytic etching of semiconductors is the occurrence of rectifying barriers. Barrier effects for germanium will be described; those for silicon are qualitatively similar.

The voltage-current curves for anodic n-type and p-type germanium

in 10 per cent KOH are shown in Fig. 1. The concentration of KOH is not critical and other electrolytes give similar results. The voltage drop for the p-type specimen is small. For anodic n-type germanium, however, the barrier is in the reverse or blocking direction as evidenced by a large voltage drop. The fact that n-type germanium differs from p-type germanium only by very small amounts of impurities suggests that the barrier is a semiconductor phenomenon and not an electrochemical one. This is confirmed by the light sensitivity of the n-type voltage-current characteristic. Fig. 2 is a schematic diagram of the arrangement for obtaining voltage-current curves. A mercury-mercuric oxide-10 per cent KOH reference electrode was used at first, but a gold wire was found equally satisfactory. At zero current, a voltage V_0 exists between the germanium and the reference electrode; this voltage is not included in Fig. 1.

The saturation current I_s, measured for the n-type barrier at a *moderate* reverse voltage (see Fig. 1), is plotted as a function of temperature in Fig. 3. The saturation current increases about 9 per cent per degree, just as for a germanium p-n junction, which indicates that the

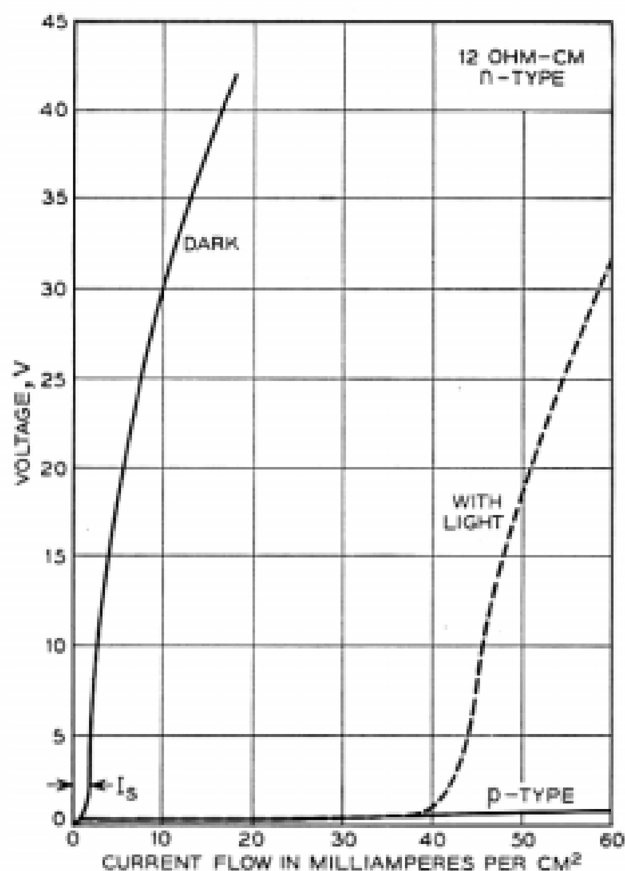

Fig. 1 — Anodic voltage-current characteristics of germanium.

current is proportional to the equilibrium density of minority carriers (holes). The same conclusion may be drawn from Fig. 4, which shows that the saturation current is higher, the higher the resistivity of the n-type germanium. But the breakdown voltages are variable and usually much lower than one would expect for planar p-n junctions made, for example, by alloying indium into the same n-type germanium.

Breakdown in bulk junctions is attributed to an avalanche multiplication of carriers in high fields.[6] The same mechanism may be responsible for breakdown of the germanium-electrolyte barrier; low and variable breakdown voltages may be caused by the pits described below.

The electrolyte-germanium barrier exhibits a kind of current multiplication that differs from high-field multiplication in two respects: it occurs at much lower reverse voltages and does not vary much with voltage.[7] This effect can be demonstrated very simply by comparison with a metal-germanium barrier, on the assumption that the latter has a current multiplication factor of unity. This assumption is supported by experiments which indicate that current flows almost entirely by hole flow, for good metal-germanium barriers.[8]

The experimental arrangement is indicated in Fig. 5(a) and (b). The voltage-current curves for an electrolyte barrier and a plated barrier on the same slice of germanium are shown in Fig. 5(c).* The curves for the

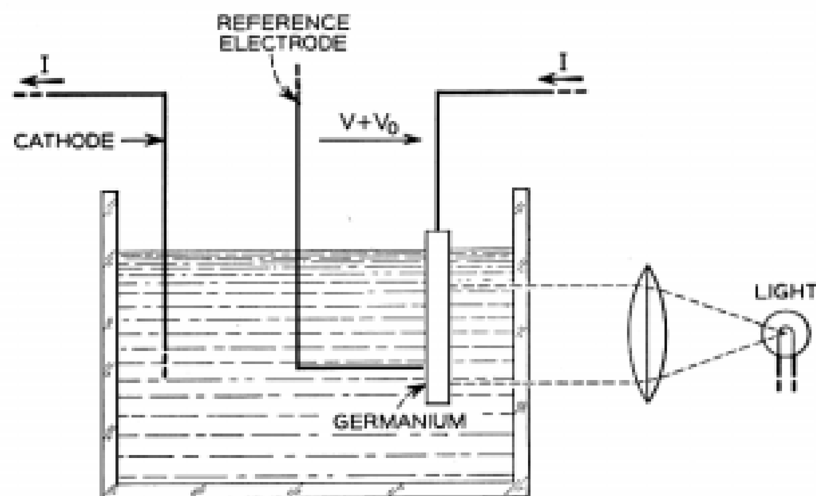

Fig. 2 — Arrangement for obtaining voltage-current characteristics.

* In Fig. 5 the dark current for the plated barrier is much larger than can be explained on the basis of hole current; it is even higher than the dark current for the electrolyte barrier, which should be at least 1.4 times the hole current. This excess dark current is believed to be leakage at the edges of the plated area and probably does not affect the intrinsic current multiplication of the plated barrier as a whole.

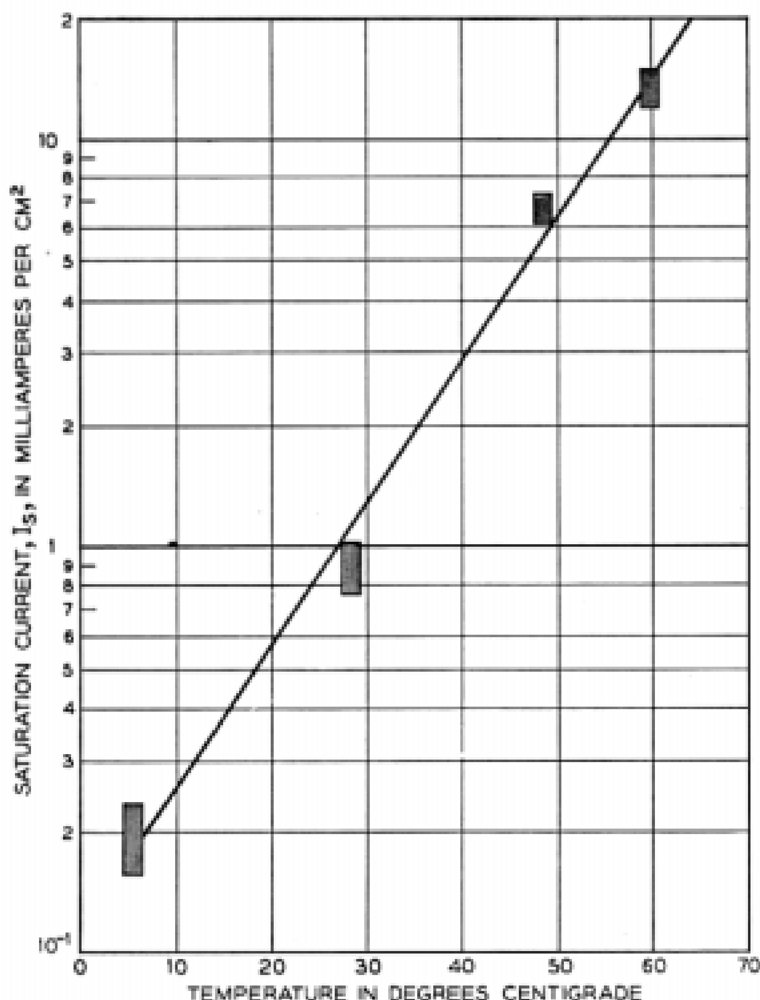

Fig. 3 — Temperature variation of the saturation current of a barrier between 5.5 ohm-cm n-type germanium and 10 per cent KOH solution.

illuminated condition were obtained by shining light on a dry face of a slice while the barriers were on the other face. The difference between the light and dark currents is larger for the electrolyte-germanium barrier than for the metal-germanium barrier, by a factor of about 1.4.

The transport of holes through the slice is probably not very different for the two barriers. Therefore, a current multiplication of 1.4 is indicated for the electrolyte barrier. About the same value was found for temperatures from 15°C to 60°C, KOH concentrations from 0.01 per cent to 10 per cent, n-type resistivities of 0.2 ohm-cm to 6 ohm-cm, light currents of 0.1 to 1.0 ma/cm^2, and for 0.1N indium sulfate.

Evidently the flow of holes to the electrolyte barrier is accompanied by a proportionate return flow of electrons, which constitutes an additional electric current. Possible mechanisms for the creation of the electrons will be discussed in a forthcoming article.[9]

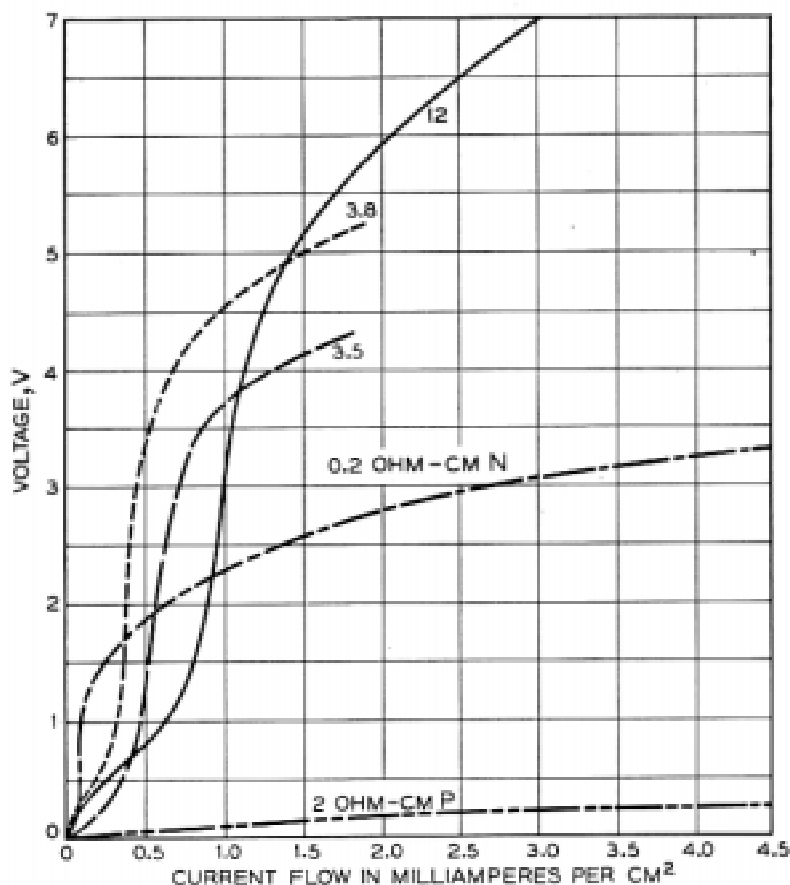

Fig. 4. — Anodic voltage-current curves for various resistivities of germanium.

SCRATCHES AND PITTING

The voltage-current curve of an electrolyte-germanium barrier is very sensitive to scratches. The curves given in the illustrations were obtained on material previously etched smooth in CP-4, a chemical etch.* [10]

If, instead, one starts with a lapped piece of n-type germanium, the electrolyte-germanium barrier is essentially "ohmic;" that is, the voltage drop is small and proportional to the current. A considerable reverse voltage can be attained if lapped n-type germanium is electrolytically etched long enough to remove most of the damaged germanium. However, a pitted surface results and the breakdown voltage achieved is not as high as for a smooth chemically-etched surface.

The depth of damage introduced by typical abrasive sawing and lapping was investigated by noting the voltage-current curve of the

* Five parts HNO_3, 3 parts 48 per cent HF, 3 parts glacial acetic acid, $\frac{1}{10}$ part Br_2.

electrolyte-germanium barrier after various amounts of material had been removed by *chemical* etching. After 20 to 50 microns had been removed, further chemical etching produced no change in the barrier characteristic. This amount of material had to be removed even if the lapping was followed by polishing to a mirror finish. The voltage-current curve of the electrolyte-germanium barrier will reveal localized damage. On the other hand, the photomagnetoelectric (PME) measurement of

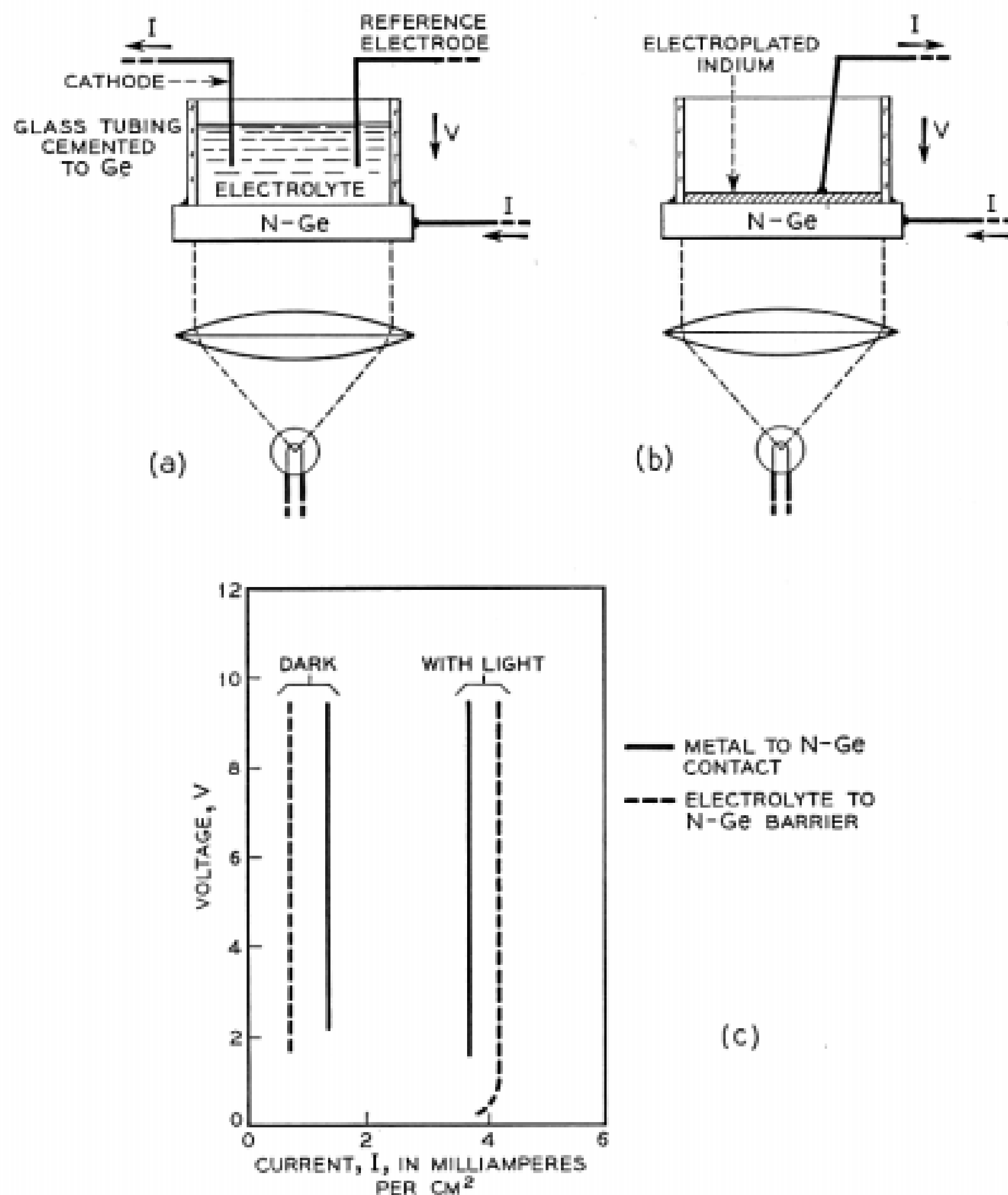

Fig. 5 — Determination of the current multiplication of the barrier between 6 ohm-cm n-type germanium and an electrolyte.

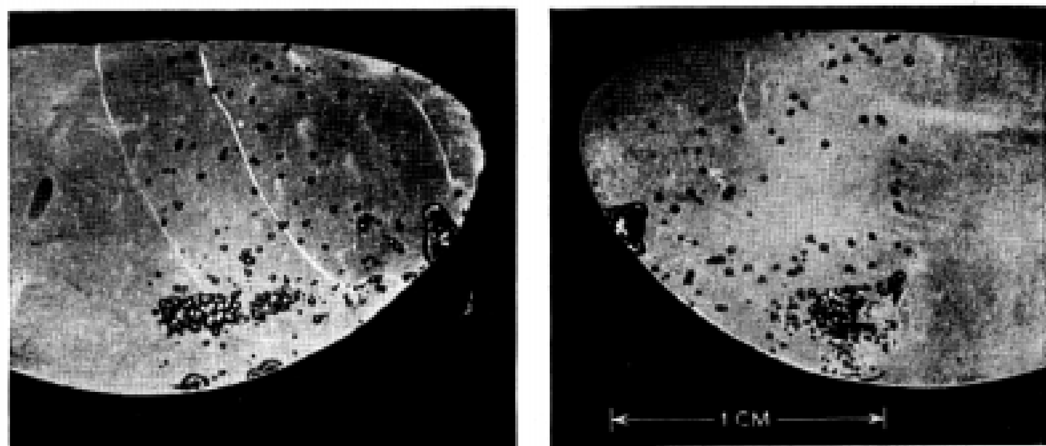

Fig. 6 — Electrolytic etch pits on two sides of 0.02-inch slice of n-type germanium. Half of the slice was in contact with the electrolyte.

surface recombination velocity gives an evaluation of the average condition of the surface.[11] A variation of the PME method has been used to study the depth of abrasion damage; the damage revealed by this method extends only to a depth comparable to the abrasive size.[12]

A scratch is *sufficient* to start a pit that increases in size without limit if anodic etching is prolonged. However, a scratch is not *necessary*. Pits are formed even when one starts with a smooth surface produced by chemical etching. A drop in the breakdown voltage of the barrier is noticed when one or more pits form. The breakdown voltage can be restored by masking the pits with polystyrene cement.

Evidence that the spontaneous pits are caused by some features of the crystal, itself, was obtained from an experiment on single-crystal n-type germanium made by an early version of the zone-leveling process. A slice of this material was electrolytically etched on both sides, after preliminary chemical etching. Photographs of the two sides of the slice are shown in Fig. 6. Only half of the slice was immersed in the electrolyte. The electrolytic etch pits are concentrated in certain regions of the slice — the same general regions on both sides of the slice. It is interesting that radioautographs and resistivity measurements indicate high donor concentrations in these regions. Improvements, including more intensive stirring, were made in the zone-leveling process, and the electrolytic etch pit distribution and the donor radioautographs have been much more uniform for subsequent material.

Several pits on a (100) face are shown in Fig. 7. The pits grow most rapidly in ⟨100⟩ directions and give the spiked effect seen in the illustration. After prolonged etching, the spikes and their branches form a complex network of caverns beneath the surface of the germanium.

High-field carrier generation may be responsible for pitting. A locally

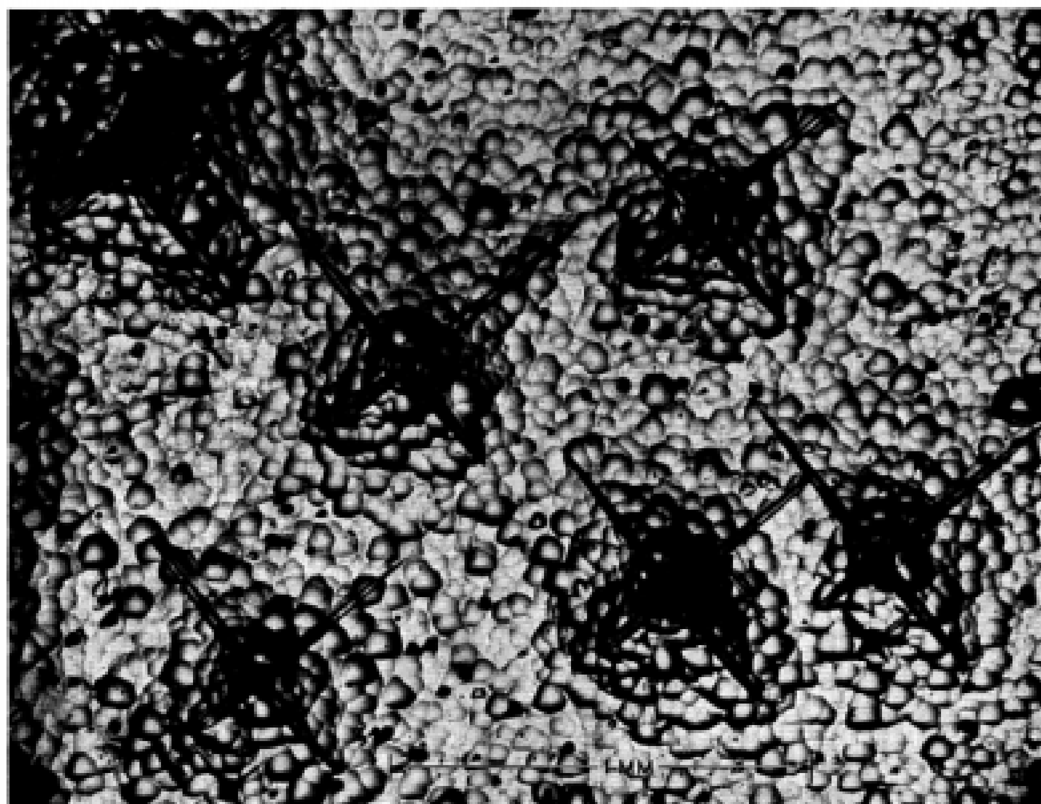

Fig. 7 — Electrolytic etch pits on n-type germanium.

high donor concentration would favor breakdown, as would any concavity of the germanium surface (which would cause a higher field for a given voltage). Very high fields must occur at the points of spikes such as those shown in Fig. 7. The continued growth of the spikes is thus favored by their geometry.

Microscopic etch pits arising from *chemical* etching have been correlated with the edge dislocations of small-angle grain boundaries.[13] A specimen of n-type germanium with chemical etch pits was photomicrographed and then etched electrolytically. The etch pits produced electrolytically could not be correlated with the chemical etch pits, most of which were still visible and essentially unchanged in appearance. Also, no correlation could be found between either kind of etch pit and the locations at which copper crystallites formed upon immersion in a copper sulfate solution. Microscopic electrolytic etch pits at dislocations in p-type germanium have been reported in a recent paper that also mentions the deep pits produced on n-type germanium.[14]

Electrolytic etch pits are observed on n-type and high-resistivity silicon. These etch pits are more nearly round than those produced in germanium.

In spite of the pitting phenomenon, electrolytic etching is success-

fully used in the fabrication of devices involving n-type semiconductors. Pitting can be reduced relative to "normal" uniform etching by any agency that increases the concentration of holes in the semiconductor. Thus, elevated temperatures, flooding with light, and injection of holes by an emitter all favor smooth etching.

SHAPING BY MEANS OF INJECTED CARRIERS

Hole-electron pairs are produced when light is absorbed by semiconductors. Light of short wavelength is absorbed in a short distance, while long wavelength light causes generation at considerable depths. The holes created by the light move by diffusion and drift and increase the current flow through an anodic electrolyte-germanium barrier at whatever point they happen to encounter the barrier. In general, more holes will diffuse to a barrier, the nearer the barrier is to the point at which the holes are created. For n-type semiconductors, the current due to the light can be orders of magnitude greater than the dark current, so that the shape resulting from etching is almost entirely determined by the light. As shown in Fig. 3, the dark current can be made very small by lowering the temperature.

An example of the shaping that can be done with light is shown in Fig. 8. A spot of light impinges on *one* side of a wafer of n-type germanium or silicon. The semiconductor is made anodic with respect to an etching electrolyte. Accurately concentric dimples are produced on *both* sides of the wafer. Two mechanisms operate to transmit the effect to the opposite side. One is that some of the light may penetrate deeply before generating a hole-electron pair. The other is that a fraction of the carriers generated near the first surface will diffuse to the opposite side. By varying the spectral content of the light and the depth within the

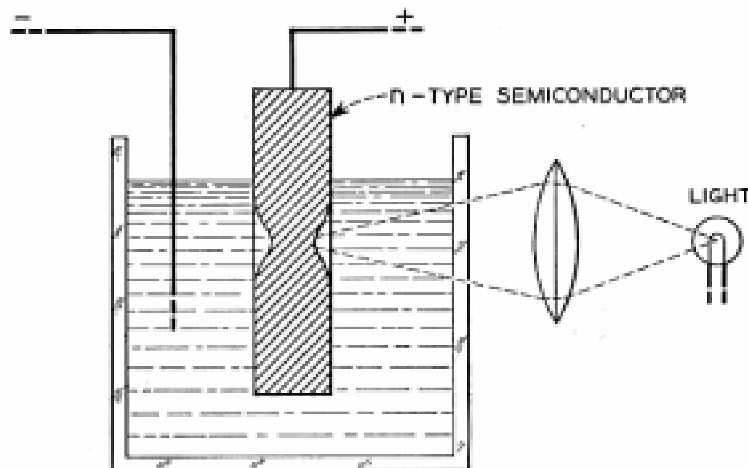

Fig. 8 — Double dimpling with light.

wafer at which the light is focused, one can produce dimples with a variety of shapes and relative sizes.

It is obvious that the double-dimpled wafer of Fig. 8 is desirable for the production of p-n-p alloy transistors. For such use, one of the most important dimensions is the thickness remaining between the bottoms of the two dimples. As has been mentioned in connection with the jet-etching process, a convenient way of monitoring this thickness to determine the endpoint of etching is to note the transmission of light of suitable wavelength.[15] There is, however, a control method that is itself automatic. It is based on the fact that at a reverse-biased p-n junction or electrolyte-semiconductor barrier there is a space-charge region that is practically free of carriers.[4] When the specimen thickness is reduced so that space-charge regions extend clear through it, current ceases to flow and etching stops in the thin regions, as long as thermally or optically generated carriers can be neglected. However, more pitting is to be expected in this method than when etching is conducted in the presence of an excess of injected carriers.

A p-n junction is a means of injecting holes into n-type semiconductors and is the basis of another method of dimpling, shown in Fig. 9. The p-n junction can be made by an alloying process such as bonding an acceptor-doped gold wire to germanium. The ohmic contact can be made by bonding a donor-doped gold wire and permits the injection of a greater excess of holes than would be possible if the current through the p-n junction were exactly equal to the etching current. Dimpling without the ohmic contact has been reported.[14]

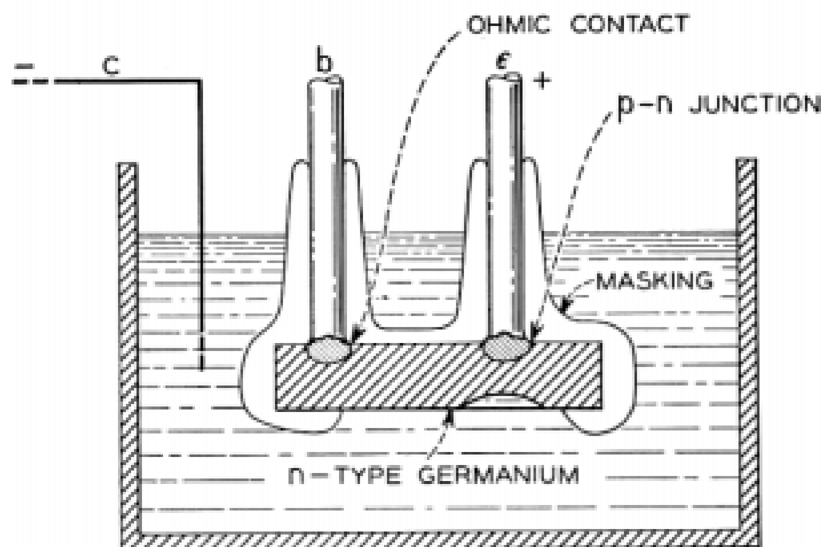

Fig. 9 — Dimpling with carriers injected by a p-n junction.

CONTROL BY OHMIC CONDUCTION

The carrier-injection shaping techniques work very well for n-type material. It is also possible to inject a significant number of holes into rather high resistivity p-type material. But what can be done about p-type material in general, short of developing cathodic etches?

The ohmic resistivity of p-type material can be used as shown in Fig. 10. More etching currect flows through surfaces near the small contact than through more remote surfaces. A substantial dimpling effect is observed when the semiconductor resistivity is equal to the electrolyte resistivity, but improved dimpling is obtained on higher resistivity semiconductor. This result is just what one might expect. But the mathematical solution for ohmic flow from a point source some distance from a planar boundary between semi-infinite materials of different conductivities shows that the current density distribution does not depend on the conductivities. An important factor omitted in the mathematical solution is the small but significant barrier voltage, consisting largely of electrochemical polarization in the electrolyte. The barrier voltage is approximately proportional to the logarithm of the current density while the ohmic voltage drops are proportional to current density. Thus, high current favors localization.

ELECTROLYTES FOR ETCHING GERMANIUM AND SILICON

The electrolyte usually has two functions in the electrolytic etching of an oxidizable substance. First, it must conduct the current necessary for the oxidation. Second, it must somehow effect removal of the oxidation product from the surface of the material being etched.

The usefulness of an electrolytic etch depends upon one or both of

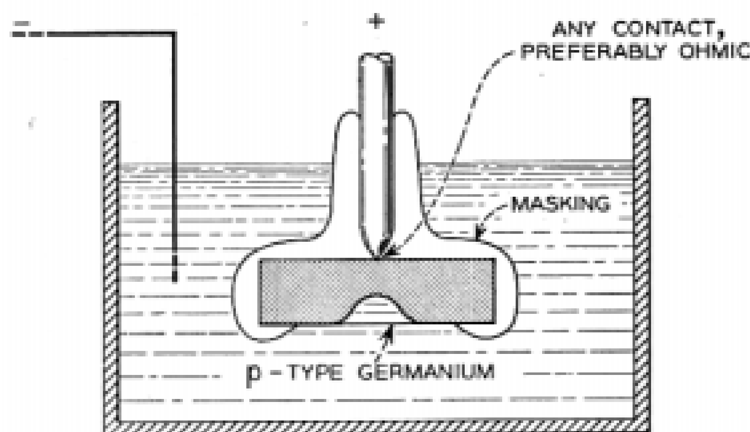

Fig. 10 — Dimpling by ohmic conduction.

the following situations — the electrolytic process accomplishes a reaction that cannot be achieved as conveniently in any other way or it permits greater control to be exercised over the reaction. Accordingly, chemical attack by the chosen electrolyte must be slight relative to the electrochemical etching.

A smooth surface is probably desirable in the neighborhood of a p-n junction, to avoid field concentrations and lowering of breakdown voltage. Therefore, a tentative requirement for an electrolyte is the production of a smooth, shiny surface on the p-type semiconductor. Such an electrolyte will give a shiny but possibly pitted surface on n-type specimens of the same semiconductor.

The effective valence of a material being electrolytically etched is defined as the number of electrons that traverse the circuit divided by the number of atoms of material removed. (The amount of material removed was determined by weighing in the experiments to be described.) If the effective valence turns out to be less than the valence one might predict from the chemistry of stable compounds, the etching is sometimes said to be "more than 100 per cent efficient." Since the anode reactions in electrolytic etching may involve unstable intermediate compounds and competing reactions, one need not be surprised at low or fractional effective valences.

Germanium can be etched in many aqueous electrolytes. A valence of almost exactly 4 is found.[16] That is, 4 electrons flow through the circuit for each atom of germanium removed. For accurate valence measurements, it is advisable to exclude oxygen by using a nitrogen atmosphere. Potassium hydroxide, indium sulfate, and sodium chloride solutions are among those that have been used. Sulfuric acid solutions are prone to yield an orange-red deposit which may be a suboxide of germanium.[16] Similar orange deposits are infrequently encountered with potassium hydroxide.

Hydrochloric acid solutions are satisfactory electrolytes. The reaction product is removed in an unusual manner when the electrolyte is about 2N hydrochloric acid. Small droplets of a clear liquid fall from the etched regions. These droplets may be germanium tetrachloride, which is denser than the electrolyte. They turn brown after a few seconds, perhaps because of hydrolysis of the tetrachloride.

Etching of germanium in sixteen different aqueous electroplating electrolytes has been mentioned.[3] Germanium can also be etched in the partly organic electrolytes described below for silicon.

One would expect that silicon could be etched by making it the anode in a cell with an aqueous hydrofluoric acid electrolyte. The seemingly

likely oxidation product, silicon dioxide, should react with the hydrofluoric acid to give silicon tetrafluoride, which could escape as a gas. In fact, a gas is formed at the anode and the silicon loses weight. But the gas is hydrogen and an effective valence of 2.0 ± 0.2 (individual determinations ranged from 1.3 to 2.7) was found instead of the value 4 that might have been expected. The quantity of hydrogen evolved is consistent with the formal reaction

$$Si \rightarrow Si^{+m} + me^{-} \qquad \text{(electrochemical oxidation)}$$

$$Si^{+m} + (4\text{-}m)H^{+} \rightarrow Si^{+4} + \tfrac{1}{2}\,(4\text{-}m)H_2 \qquad \text{(chemical oxidation)}$$

where m is about two. The experiments were done in 24 per cent to 48 per cent aqueous solutions of HF at current densities up to 0.5 amp/cm^2.

The suggestion that the electrochemical oxidation precedes the chemical oxidation is supported by the appearance and behavior of the etched surfaces. Instead of being shiny, the surfaces have a matte black, brown, or red deposit.

At 40× magnification, the deposit appears to consist of flakes of a resinous material, tentatively supposed to be a silicon suboxide. A remarkable reaction can be demonstrated if the silicon is rinsed briefly in water and alcohol after the electrolytic etch, dried, and stored in air for as long as a year. Upon reimmersing this silicon in water, one can observe the liberation of gas bubbles at its surface. This gas is presumed to be hydrogen. To initiate the reaction it is sometimes necessary to dip the specimen first in alcohol, as water may otherwise not wet it. The specimens also liberate hydrogen from alcohol and even from toluene.

Thus, chemical oxidation can follow electrolytic oxidation. But chemical oxidation does not proceed at a significant rate before the current is turned on.

Smooth, shiny electrolytic etching of p-type silicon has been obtained with mixtures of hydrofluoric acid and organic hydroxyl compounds, such as alcohols, glycols, and glycerine. These mixtures may be anhydrous or may contain as much as 90 per cent water. The organic additives tend to minimize the chemical oxidation of the silicon. They also permit etching at temperatures below the freezing point of aqueous solutions. They lower the conductivity of the electrolyte.

For a given electrolyte composition, there is a threshold current density, usually between 0.01 and 0.1 amps/cm^2, for smooth etching. Lower current densities give black or red surfaces with the same hydrogen-liberating capabilities as those obtained in aqueous hydrofluoric acid.

In general, smooth etching of silicon seems to result when the effective valence is nearly 4 and there is little anodic evolution of gas. The electrical properties of the smooth surface appear to be equivalent to those of smooth silicon surfaces produced by chemical etching in mixtures of nitric and hydrofluoric acids. On the other hand, the reactive surface produced at a valence of about 2, with anodic hydrogen evolution, is capable of practically shorting-out a silicon p-n junction. The electrical properties of this surface tend to change upon standing in air.

ACKNOWLEDGEMENTS

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