

TRANSISTOR TECHNOLOGY

VOLUME III

Edited by

F. J. BIONDI

*Member of the Technical Staff
Bell Telephone Laboratories, Inc.*



D. VAN NOSTRAND COMPANY, INC.

PRINCETON, NEW JERSEY

TORONTO

LONDON

NEW YORK

5E. PHOTOENGRAVING IN TRANSISTOR FABRICATION *

J. ANDRUS AND W. L. BOND

Photoengraving as adapted to transistor fabrication is described. Methods are given for polishing the crystal plates, cleaning and coating, exposure to light through a stencil; the developing of the image, its dyeing and the etching of the pattern into the crystal. The method produces strain-free

*The authors wish to thank G. Berry who did the cutting, grinding and polishing, and also A. A. Tartaglia for the photographs.

surfaces and allows one to use patterns too small and complicated to be cut mechanically.

Photoengraving is used commercially to etch small intricate patterns into metal plates to be used in printing diagrams for books, etc. We have adapted the art to our use in transistor fabrication, where it is often desired to cut small intricate patterns into surfaces of semiconductors. The fineness of the detail obtainable is of the order of the resolution of the microscope. This method is particularly desirable because it should leave a surface that is not strained mechanically—mechanical operations such as grinding, sawing, or scratching always leave a strained surface. A strained surface has electrical properties that are often objectionable.

After the discovery of materials that are made insoluble by exposure to light, photoengraving was possible. One could coat the surface to be engraved with this material and expose it to light through a stencil. The part protected from the light by the stencil is then soluble and can be dissolved away by a liquid that cannot dissolve the part of the coating that has been exposed to light. A corrosive fluid that can etch the surface to be engraved but cannot attack the protective coating can now etch a pattern resembling the stencil. Those who perfected the art for the printing industry had to learn how to polish and clean metal plates (copper and zinc are used) so that the corrosive fluid would bite in uniformly. They also had to find corrosive fluids (etchants) that would attack the metal but not the coating. In the photoengraving trade the coating is called *resist*.

Silicon and germanium being so different from copper and zinc, these problems had to be solved anew. Hence we describe how the material is polished, how it is cleaned, how it is coated, exposed, developed, dyed and etched. Also we mention how negatives for the final printing are made. These are more properly called stencils to avoid such oddities as printing negatives directly from negatives in case two steps are used in the preparation of the final stencil. The stencil is generally a photographic film or plate carrying the proper pattern.

The photoengraving technique is not limited to etching processes. One can evaporate metal over a developed image and then dissolve away the coating. This leaves metal only on the areas that were bare because the evaporated metal that fell on the coating breaks away when its base is dissolved. The metal coat can be plated on electrolytically or deposited chemically instead of being evaporated onto the surface. Also one can use the photoengraving method to uncover a protective coating according to a pattern. This protective coating can be dissolved away where exposed but will be chosen to withstand certain etchants better than does the resist. There are many other possible variations.

PREPARATION OF THE SPECIMEN

Since we wish to make very small patterns, the surfaces must be quite flat, otherwise the stencil will not lie everywhere snugly against the surface. Wherever there is a gap between stencil and surface, light can creep under the stencil. This makes the line positions and widths uncertain. Also we need a scratch-free surface because the etchants attack faster on scratches, making the surface uneven.

After a semiconductor crystal is sawed into a plate, one surface of the plate is lapped on cast iron with #600 grit Carborundum (Ref. 1) in water to remove the saw marks and to secure a flat surface. The crystal plate is then cemented, lapped surface down on an adjustable jig, Fig. 1.



FIG. 1 Adjustable jig used in lapping and polishing of semiconductor plates.

By using this jig, it is possible to get and maintain parallelism. The jig also enables one to lap and polish the plate to a given thickness. The exposed surface of the plate is now lapped with #600 grit Carborundum (Ref. 1). Pits or grind marks are left on the surface from the #600 grit Carborundum (Ref. 1) to a depth of about $25\ \mu$ or 0.001 in.

The #600 grit-lapped surface is then lapped with #303½ emery on a glass or quartz lap. The laps should be checked frequently for flatness; quartz laps remain flat for longer periods of use than do glass laps. Use of a quartz or glass lap minimizes metal contamination and reduces scratches. Lapping with #303½ emery is continued until all of the pits left by the #600 grit are removed. The pits left by the #303½ are about $12\ \mu$ deep and are removed with #305 emery which leaves pits of about $5\ \mu$ and probably leaves a disturbed layer of another $5\ \mu$. Therefore about $10\ \mu$ must be removed from the surface in the polishing process.

Great care should be used to prevent carrying coarser grits on to the later finer stages of grinding and polishing. The hands should be carefully washed before picking up the jig, and the jig and crystal should be washed carefully before placing on the grinding or polishing machine. The polishing lap and all of the polishing equipment should be covered



FIG. 2 Bowl feed polisher. (American Optical Co.)

at all times when not in use. One speck of grit can ruin an otherwise perfectly polished surface. By exercising great care in cleanliness we have been able to polish silicon crystal plates down to 0.0005 in. in thickness, polishing both sides of the plate.

The crystal plate is now ready for polishing. The rough polishing is done on a rotating plastic lap made of block (Teflon or nylon) using Linde A (Ref. 2) levigated alumina. The machine that rotates the lap is the American Optical Company Bowlfeed Polisher (#1M-423A). This machine turns the lap, holds the jig so that it may spin, and oscillates it in and out from the lap center. It also keeps a steady stream of the

polishing fluid pouring onto the lap. The machine has a time switch which reduces the amount of attention required (Fig. 2). To keep the fine Linde A (Ref. 2) powder in suspension in water, $\frac{1}{3}$ volume of bentonite clay is added to the Linde A (Ref. 2) and water added to a creamy consistency. The rough polishing takes from 30 min to an hour for a 2 cm² surface.

Final polishing is done on a rayon-cloth-covered lap, Fig. 3, that has



FIG. 3 Final polishing with $\frac{1}{2}\mu$ diamond abrasive on rayon covered lap.

been impregnated with $\frac{1}{2}\mu$ grit size diamond paste. This final polish takes but 2 or 3 min. We know that, after the final polish, the crystal surface may have a disturbed layer of the order of a few microns. This work-strained surface layer can be removed from germanium with a 5 sec etch in Super X 1114 etchant (see *etching*, below) and still maintain a flat surface.

Cleanliness is a very important factor in the final lapping and even more so in the final polishing. One particle of the #305 emery, whose particle size is about 5 μ , will mean a scratch of that magnitude on the surface plus another few microns of disturbed material under the scratch which would only show up after etching. That is the reason we stress the point of cleanliness. Finally the crystal plate is washed in trichloroethylene, rinsed in deionized (or distilled) water, and dried on lint-free paper or blown dry with filtered air.

APPLICATION AND PROCESSING OF THE PHOTO RESIST

A small amount of Eastman's Photo Resist (KPR) solution is filtered through filter paper into a clean glass container. The plates are placed in a vacuum holder and are coated using a small sable brush (Fig. 4). If too much solution is put on, it will have a tendency to form a bead at the edges. Therefore, care must be exercised to coat the plate with only

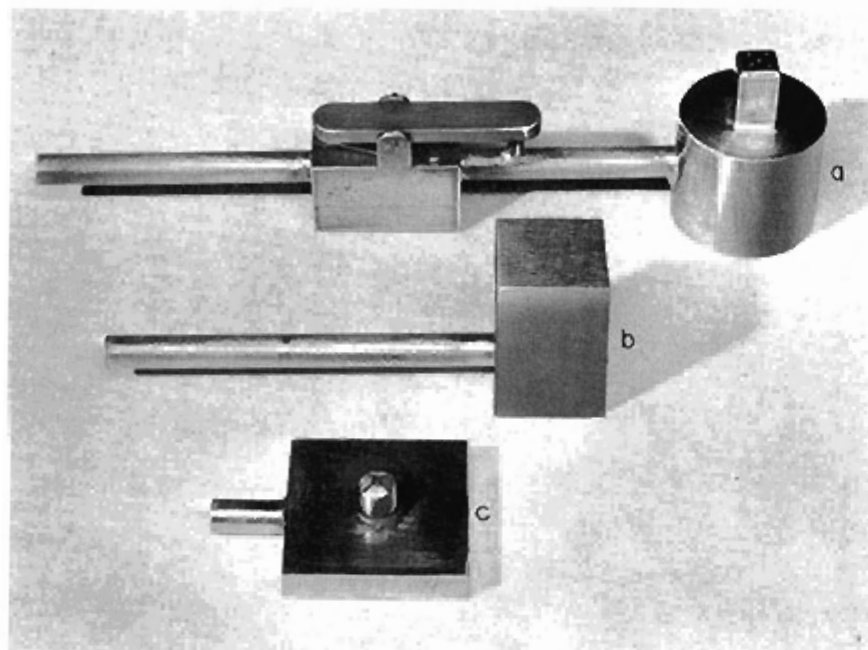


FIG. 4 Vacuum holder used for holding small plates while photo resist is being applied, and also while plates are being dyed and washed after development. (a) Release valve; (b) holder for six plates; and (c) single holder.

a thin uniform coating. Plates are then air dried at room temperature for about 10 min or held about 8 in. from a 250-watt infrared heat lamp for 3 to 5 min.

Photo Resist is extremely sensitive to ultraviolet radiation, but rather insensitive to tungsten illumination; therefore, care must be taken not to expose resist-coated plates to daylight since even a few seconds' exposure to white light will fog the resist. The stencil is placed on the glass part of a vacuum contact frame (Fig. 5) with the emulsion side up. The crystal plate is placed coated side down making intimate contact with the negative. The vacuum frame is then closed and the plates are exposed to a 20-amp double-arc lamp for 3 min (average time) about 30 in. from the lamp.

After exposure the crystal plates are removed from the vacuum frame

and placed in a developing solution (purchasable from the supplier of KPR) at room temperature, using intermittent agitation. The resist is not touched with anything solid, as it is soft during development. A few minutes' development is sufficient, but the image will not be overdeveloped by remaining hours in the developer.

Since the resist is transparent, visual inspection of the image is impossi-

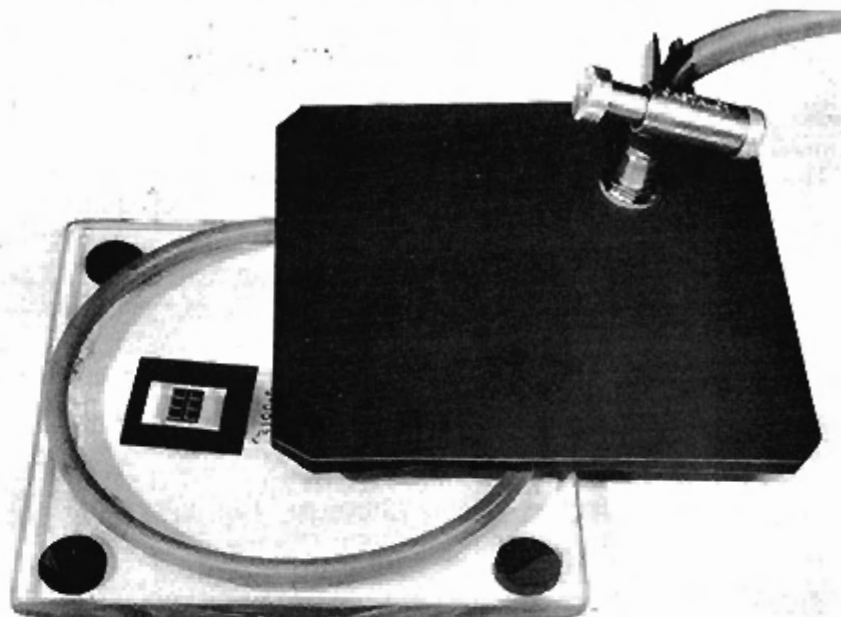


FIG. 5 Six crystal plates $\frac{1}{8}$ -in. sq being prepared for exposure. When rubber diaphragm is put in place over negative and plates, the frame is evacuated, pulling the crystal plates firmly against the negative.

ble unless the resist is dyed some dark color. A few drops of black dye (obtainable from the supplier of KPR) are put on the surface of the crystal with a medicine dropper immediately after development and while the crystal is still wet and allowed to remain on for one minute. While the dye is still wet, the plate is held under a running stream of distilled or deionized water at 65–75°F for one minute. In this wash the part of the resist that was not exposed to light is dissolved. The remaining photo resist image is still soft at this stage and should be carefully handled. It is dried by placing coated side down on clean absorbent filter paper or lint-free blotting paper. This step is intended to remove only the visible moisture.

Inspection under a microscope shows whether the image is likely to produce a satisfactory engraving. If there are a few specks of dust they may be removed by gentle rubbing with a bit of cotton on the end of a toothpick, the cotton being dipped in distilled water.

The plate is then baked in an oven at 150°C for about 10 min to harden the resist. After curing the resist, the plates are ready for etching, plating, chemical depositing, or vapor coating of metals.

ETCHING

Using an electrolytic etch we were able to preserve the resist, but did not get uniform removal of the crystal surface. The etching action seemed to work more rapidly around the edges of the bare areas and less rapidly in the center of such areas. Also, the many other variables such as current density, temperature, resistivity of crystal, etc., made the electrolytic process look unattractive.

However, a very constant etching rate and uniform cut were obtained on germanium using the formulas listed below, at room temperature.

SUPER X-1114 FOR GERMANIUM. Components: 1 part by volume Nitric (HNO_3); 1 part by volume Superoxol 30 per cent (H_2O_2); 1 part by volume Hydrofluoric 48 per cent (HF); 4 parts by volume distilled water.

ETCH FORMULA FOR SILICON. Silver-Glycol etch is made up in two separate polyethylene plastic containers designated A and B.

A	400 cc HNO_3	Nitric Acid
	10 cc HF	Hydrofluoric Acid
	10 cc AgNO_3	Silver Nitrate Solution (1 gm AgNO_3 dissolved in 100 cc of H_2O)
B	200 cc H_2O	Distilled Water
	200 cc	Propylene Glycol

1) Mix 1 part A to 1 part B just before etching, using a polyethylene or platinum container.

2) Place container into a pan of cool tap water to bring the temperature of etch to room temperature 24°C. This takes about 5 min.

3) Place crystal to be etched in container and periodically brush over surface gently with a sable or camel's hair brush to remove any bubbles that may form on the surface. The brushes to be used are Chinese sable mounted in bamboo. Brushes mounted in metal should not be used since the etchant will attack the metal and may also contaminate the surface.

Precautionary measures must be taken in the storage of the acids. HF , HNO_2 , and AgNO_3 can safely be mixed and stored together in a polyethylene bottle, but never mix the propylene glycol into the same container that contains the acids for storage. A mixture of the propylene glycol and acids causes a chemical reaction that liberates gases, causing pressure to build up to the extent of exploding, if the bottle has a screw-type stopper. Mixing and storage instructions, therefore, should be very carefully followed.

The etching rate of the silver-glycol etch for silicon is shown in Fig. 6. There was no noticeable change in the rate after storage of the mixture in polyethylene bottles for periods of two months.

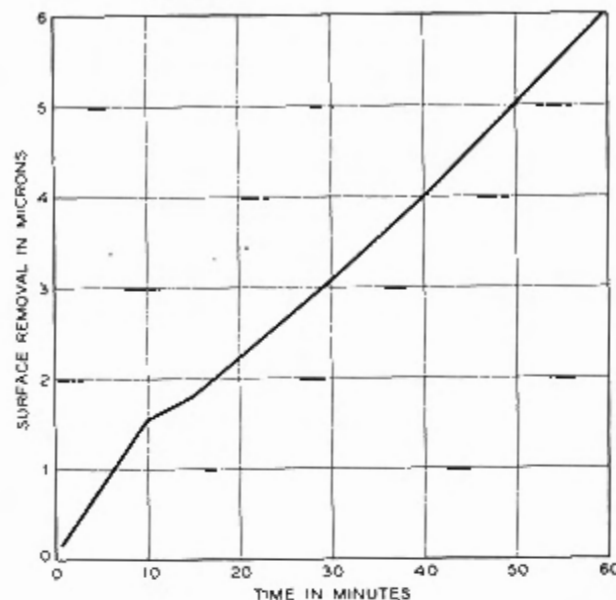


FIG. 6 Etching rate of silicon for silver glycol etch.

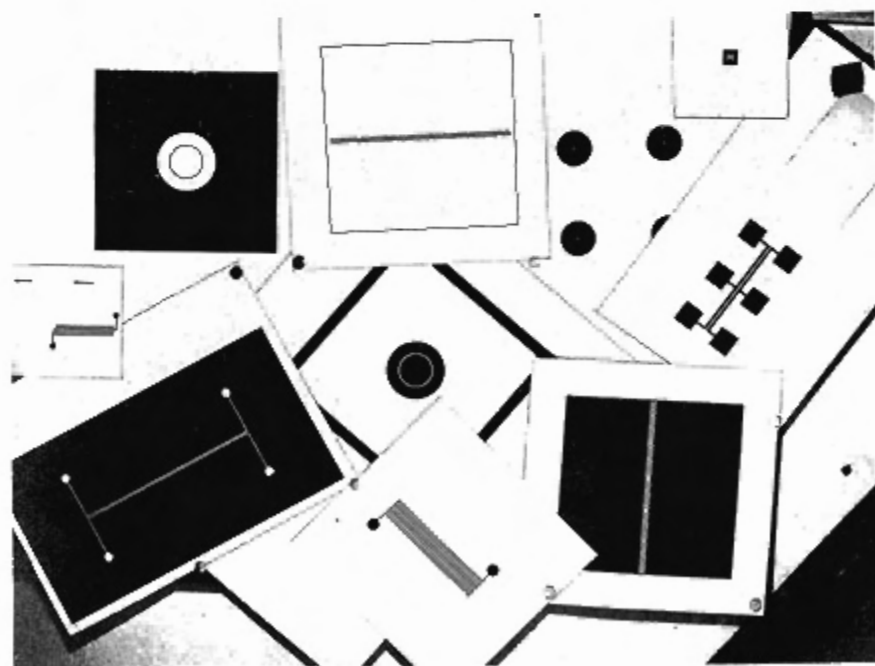


FIG. 7 Geometric patterns used for making negative stencils. These drawings, in most cases, were reduced 40 and 80 to one, most lines were reduced to 0.001 in. or less.

We have worked with germanium of various resistivities and several orientations in our etch tests. A very constant etching rate and uniform cut were obtained using the Super X-1114 formula in all cases. The difference in the rates between the (110), (111) and (100) surfaces was so slight that it is negligible. Twenty-five microns (0.001 in.) were removed in 3 min and 20 sec or 2.5 microns ($\frac{1}{10}$ mil) in 20 sec, etching a surface

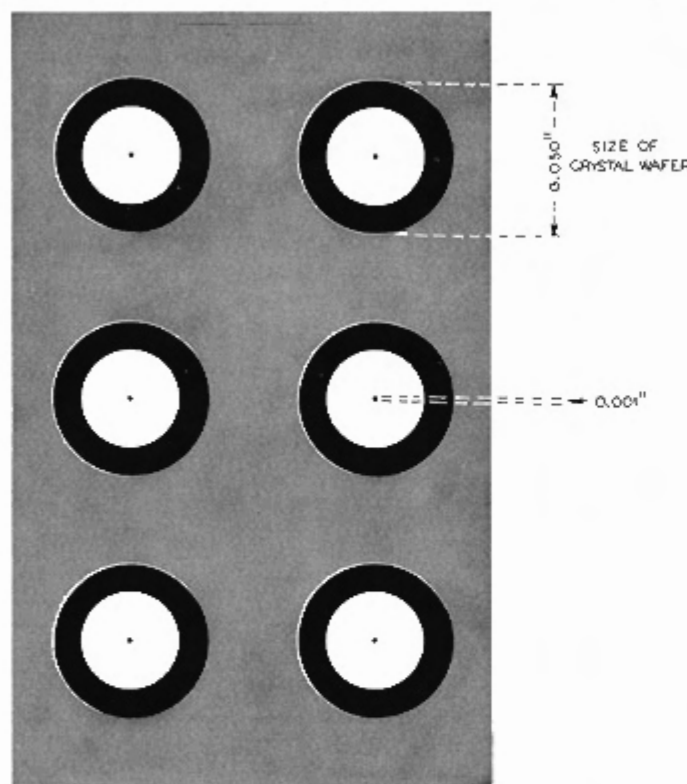


FIG. 8 Stencil for printing pattern on six semiconductors simultaneously.

$\frac{1}{8}$ in. square. There was no noticeable difference in enlarging or decreasing the area by a factor of two.

Nitric acid and the Superoxol act as oxidizing agents, with hydrofluoric acid as the oxide solvent. The water controls the etch rate and also acts as a coolant, preventing too violent etching action by controlling the temperature.

REMOVING THE RESIST

To remove the resist, the plates are immersed in Cellosolve (Ref. 3) acetate for about 10 min, and then the face of the plate is swabbed gently with a bit of cotton on a toothpick. This solvent penetrates the resist even through a thin film of evaporated or chemically deposited

metal. This allows us to remove the metal with the resist without disturbing the metal which fell on bare substrate.

STENCIL PREPARATION

A drawing of the desired pattern is made in black and white and is reduced photographically to make the stencil. For lines finer than a few

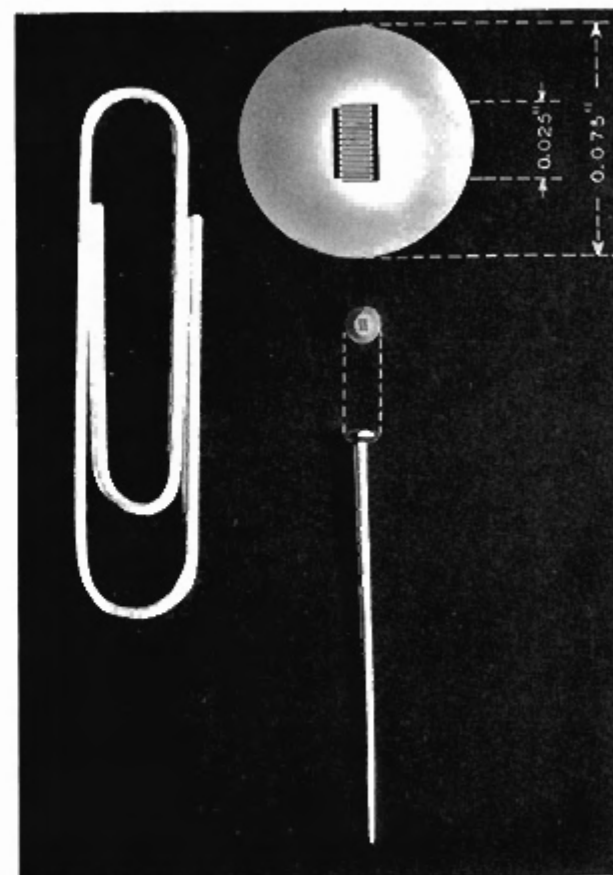


FIG. 9 Pattern compared with head of a pin.

mils, Reprolith film is used. A process lens should be capable of giving lines about $\frac{3}{4}$ mil wide. For lines down to about a micron, one can use microscope objectives in reverse.

RESULTS

Fig. 7 shows some geometric patterns that have been drawn in black and white, greatly reduced photographically and reproduced on germanium surfaces and then covered with evaporated metal, chemical

deposit, and surface diffused layers. While this work is still in the experimental stage, it has proved itself to be a feasible method of reproduction and appears readily adaptable for production on a large scale. Fig. 8 shows a drawing of a photographic stencil or "negative" for reproducing a design onto a half dozen germanium wafers simultaneously. Fig. 9 shows a photograph of a miniaturized pattern in comparison with the head of a pin.

It should be noted that this procedure is presently used only in Bell Telephone Laboratories developmental work.

REFERENCES

1. Trade name of Carborundum Co., Buffalo, N. Y.
2. Trade name of Linde Air Products Co., Inc., N. Y. C., N. Y.
3. Trade name of Union Carbide and Carbon Chemical Co., N. Y. C., N. Y.

M. V. SULLIVAN AND R. M. WARNER, JR.

Chapter 6

OHMIC CONTACTS TO SILICON AND GERMANIUM

An ohmic contact to a semiconductor device has been described as a contact which delivers current to the device without entering into an active process. A number of techniques for making such contacts are reviewed; these employ alloys, preforms, evaporated films, powdered-conductor suspensions, liquid metals, electroplates, displacement plates, and electroless plates. The resulting contacts are appraised primarily in terms of their mechanical strength and their electrical resistance.

Electrical contacts are essential parts of any usable semiconductor device. Contacts may be conveniently divided into two classes, rectifying and non-rectifying. The purpose of this chapter is to bring together a number of the methods that have been used to make non-rectifying or ohmic contacts to either germanium or silicon so that the design engineer may make a reasonable choice of the available techniques.*

Many commonly used ohmic contacts rectify slightly; the amount of rectification that can be tolerated depends upon the specific situation. For example, if the contact can be placed several diffusion lengths from a reverse-biased junction, then most of the minority carriers which may be injected will recombine before they can be collected. Another means which has been widely used to achieve the same end is the placement of a region of high recombination rate between the metallic contact and the semiconductor body. This can be accomplished by sandblasting the semiconductor surface before applying the contact. It should be understood that under certain conditions, for example, where low contact resistance is desired, even a small amount of rectification may be undesirable.

In the case of alloyed or bonded contacts to germanium it is possible to approach a linear current-voltage characteristic more closely and to

* A definition and general discussion of ohmic contacts is given in *Transistor Technology*, Vol. I, D. Van Nostrand Company, Inc., Princeton, N. J., 1957, Chapters 14 and 15.