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The Effect of Surface Treatments on Point-Contact Transistor Characteristics

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A description is given of the electrical properties of formed point contacts on germanium. A useful technique for observation of the equipotentials surrounding such contacts is described. The contrasting properties of donor-free and donor-doped contacts, used as diodes or transistor collectors are emphasized.

It is shown that unformed point contacts (which have electrical properties largely determined by a surface barrier layer), may exhibit analogous differences. Such changes are produced by chemical treatments calculated to influence properties of a soluble germanium oxide film on the surface.

The above information is applied to a study of transistor forming as it is done in present point-contact transistor processing. It is shown that high yields from the forming process can be expected on oxidized surfaces, and that chemical washes which remove soluble germanium oxide drastically lower forming yields. These and other effects are evaluated as sources of variability in forming yield.

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1. INTRODUCTION

The point-contact transistor, on the basis of several years use in the field in Bell System applications, has proved itself to be rugged and dependable. For certain military applications, a lasting demand exists for high-speed point-contact transistors. The adaptation of cartridge type units to a hermetically sealed structure has been completed, with further benefits to reliability. To date, the point-contact transistor is one of the few transistors to successfully pass all military specifications for shock, vibration, and high acceleration. Thus, although there are at present limitations to the electrical characteristics that can be built into a point-contact transistor which make it unsuitable for use in some switching circuits, there are many applications in which this type of transistor can give consistent and reliable performance. In fact, applications exist wherein the specific requirements are uniquely satisfied by the point-contact transistor.

However, the basic operational principles of this kind of device are not as well understood as would be desirable for facilitating developmental studies for manufacture. Although considerable effort has been

expended towards the analysis and understanding of the physical mechanisms of the point-contact transistor since its announcement in 1948, a complete design theory for these transistors is not available. This lack probably results partially from a more general interest in the readily designable junction transistor types, and partially from the relative complexity of the device itself. Actually the physical mechanisms which account for the operation of this device have their counterparts in at least three basically unique devices: the point diode, the junction transistor, and the filamentary transistor.

Thus, although the empirical knowledge of point-contact transistor design and operation is large enough to allow a reasonable degree of designability, and manufacture of these transistors in large quantities is possible, there are, from time to time, manufacturing problems which are often difficult to solve without sound theoretical understanding of the physical mechanisms which make the device work.

This article is concerned with describing the results of a general study of the physical properties of a few specific kinds of point contacts. The kinds of contact studied have been those of specific interest to those concerned with manufacture and processing of point-contact transistors. This investigation was conducted in parallel with the final development for manufacture of the hermetically sealed point-contact transistor. The study of these properties has led to practical solutions of several problems encountered during manufacture of point-contact transistors, and has provided experimental data which is of interest in consideration of the basic physical mechanisms involved in the operation of the point-contact transistor.

The work to be described, primarily experimental in nature, follows in Sections 2, 3 and 4. In section 2, the properties of formed, or electrically pulsed point contacts, and their relation to the source of output characteristic anomalies often responsible for lowering forming yields in point-contact transistor production is discussed. The properties of point contacts which have received no electrical forming in the conventional sense are considered in section 3. The electrical properties of these contacts, used as diodes or transistor collectors, are shown to be dependent on chemical history of the etched germanium surface. Thus "chemical forming" of point contacts is possible. Section 4 deals with application of these results to forming problems which arise during manufacture of point-contact transistors. The important relation between the chemical history of the surface and the forming on that surface is considered.

2. PROPERTIES OF FORMED POINT CONTACTS

2.1 *Effects of Electrical Forming on Point Contacts*

The simplest form of point-contact transistor collector is a metal to semiconductor contact which has not been subjected to excessive power dissipation either in short high energy pulses, or in the form of more prolonged aging at lower power levels. Such contacts will be referred to as unformed contacts, and their properties will be discussed in detail in Section 3. Unformed point-contact transistors sometimes exhibit power gain, but in general they are not suitable for use as active devices because the gain, although it may be highly variable from unit to unit, is usually low. The electrical characteristics of such contacts depend on a metal-semiconductor contact at the semiconductor surface, and control of these properties requires exacting control of surface preparation, surrounding ambient, and mechanical stability of the point.

In early experiments, Brattain[1] used electrical forming to improve both the power gain and stability of the transistor. For present purposes, the process of electrical forming will be defined as the passage of a short pulse of reverse current through a point contact which produces permanent changes in the electrical properties of the contact. This is usually accomplished by charging a condenser to several hundred volts, and subsequently discharging it through a resistor in series with the transistor collector. Bardeen and Pfann,[2] investigating electrical forming of phosphor bronze points on etched germanium surfaces, indicate, as a possible explanation of their data, that the forming pulse changes the height of the potential barrier at the germanium surface. This would, in absence of large surface conductivity, increase the reverse current through the point and increase the efficiency of hole collection by the point.[3] Thus, the formed point may, according to theory,[4] act as a collector with a current multiplication (α) greater than unity. Thermal and potential probing of an n-germanium surface under a formed phosphor bronze point indicates, according to Valdes,[5] that an appreciable volume of germanium is converted to p-type conduction. Thus, the reverse current through a formed point probably depends on the characteristics of a p-n junction a small distance from the point, rather than on a potential barrier at the germanium surface.

A characteristic of the point-contact transistor is that the current gain can be substantially greater than unity. The current gain, α, is usually defined as the current multiplication at constant voltage, that is:

$$\alpha = -\frac{\partial I_c}{\partial I_e}\bigg|_{V_c} \tag{1}$$

where I_c and I_e are the collector and emitter currents. The α can be considered as the product of three terms, that is:

$$\alpha = \alpha_i \beta \gamma \tag{2}$$

where γ and β represent the injection efficiency and transport factor respectively for minority carriers. The term α_i is the "intrinsic" current multiplication of the collector itself. As mentioned above, there are theoretical reasons to account for an α_i as large as $(1 + b)$, where b is the ratio μ_n/μ_p of the mobilities of electrons and holes, and thus the term α_i may be roughly as large as 3.1. The average current gain, $\bar{\alpha}$, taken over a large interval of emitter current, is seldom found to be greater than this value, and is usually about 2.5. However, the small signal α at low emitter current usually is found to be considerably larger than 3.1.

Several mechanisms have been proposed to account for this excess current gain at low emitter bias in formed transistors. The most generally known of these are the p-n hook hypothesis and the trapping model.[6, 7]

The experiments to be described in this section will be concerned primarily with the characteristics of formed points as transistor collectors, and thus with the transport factor β. The subject of the origin of the intrinsic α_i will be discussed further in a later section.

The experiment of Valdes indicates that the properties of a formed point contact depend on the physical properties of a small region of germanium near the point, produced by impurity diffusion from the point or imperfections introduced during the forming pulse. A highly idealized representation of the physical situation is shown in Fig. 1. This is a radial model of a formed point contact on a semi-infinite block of n-germanium (respectively ρ), with a hemispherical p-layer (radius $\simeq r_0$). The electron and hole concentrations in the formed layer near the junction are designated as n_p and p. If a reverse bias V_c is applied to the point, a potential difference $V(r_1) - V(r_2) = V_J$ results from the resistance of the junction at r_0. For $r \geqq r_2$, at distances well outside r_0, the potential $V(r)$ and the magnitude of the field $E(r)$ are given by

$$V = \frac{\rho I}{2\pi r} \tag{3}$$

$$E = \frac{\rho I}{2\pi r^2} \tag{4}$$

where I is the total current through the point. For

$$| V_c - V(r_1) | \ll | V_J |, \; V(r_2) \simeq V_c - V_J ,$$

and the junction resistance limits the magnitude of the drift field that can be set up near the point. For example, if the lifetime τ_n of electrons in the p-layer[8] is substantially lower than τ_p, that of holes in the germanium bulk, the reverse current density across the junction can be increased by an increase in n_p, and junction resistance lowered.

Pfann[9] reports a substantial increase in the reverse current of formed point contacts with donor concentration of the point wire. The increase in n_p will depend on the distribution of donors in the p-layer after the forming pulse. A high donor concentration near the collector point may

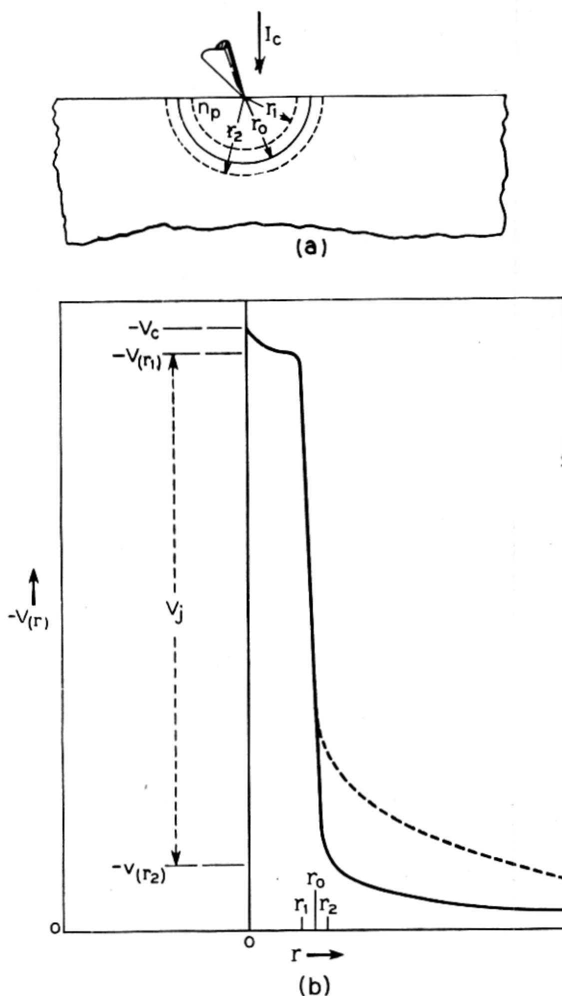

Fig. 1 — Formed point contact under reverse bias — schematic representation.

form an n-type inversion layer under the point (p-n hook) which, when the point is under reverse bias, acts as an electron emitter. Such a situation might arise as a result of diffusion of impurities from the collector point at the high temperature reached during the forming pulse. An acceptor element, such as copper, with a high diffusion coefficient[10] might penetrate substantially farther into the germanium than donor elements such as phosphorous or antimony[11] with lower diffusion constants. Thus, the donor concentration near the point might be substantially higher than the acceptor concentration if the solubility of the acceptor element is low.

On the other hand, an appreciable number of donor atoms may penetrate the germanium as far as do the acceptors. Thus, the equilibrium value of n_p may be increased simply by decreasing the effective concentration of acceptors in the p-layer. Such a case might arise when a collector point such as copper is doped with a suitable amount of a donor element with a large diffusion coefficient and limited solubility.

The observation of regions of melted germanium[12] under heavily formed points gives evidence for a somewhat different interpretation of the forming process. It has been suggested[13] that forming is essentially a remelt process. For example, forming of a phosphor-bronze point may produce a copper-germanium eutectic, allowing the introduction of a sizeable phosphorus concentration in the remelt region which is maintained after freezing. Thus the depth of penetration of the donor element depends upon the size of the remelt region, and the penetration of the acceptor element depends upon its solid state diffusion coefficient. This mechanism can lead either to the formation of a p-n hook, or at least to a lyer of p-germanium with a high equilibrium electron concentration.

Whatever the reason for the decrease in resistance of the collector barrier, if it is sufficient, the magnitude of $E(r)$ for $r > r_2$ can be increased by forming to sufficient value to ensure efficient collection of holes and a transport factor β close to unity.

It would then be expected that for a formed donor-free point, such as the beryllium-copper alloy points often used as unformed emitters, the formed p-region would have a high acceptor concentration, n_p would be small, and under reverse bias, the magnitude of V_J would be large, with $| I_{co} |$, $| V(r_2) |$, and average α small, [solid curve, Fig. 1(b). On the other hand, a formed phosphor bronze point of the kind conventionally used to make transistor collectors, should exhibit under reverse bias, a lesser magnitude of V_J, with $| I_{co} |$, $| V(r_2) |$, and α as much as an order of magnitude larger, (dashed line in Fig. 1(b)].

2.2 *Donor-Free and Donor-Doped Contacts*

The qualitative picture of the conventional formed contact given above has been substantially supported by the work of Valdes, who observed a large increase in floating potential near the reverse biased collector after the forming pulse and a substantial p-region in the bulk of the germanium after forming.

Experiments have been directed to a comparison of the properties as diodes and collectors, between two kinds of points. Phosphor bronze points of the type used as transistor collectors, and beryllium copper points, normally used as emitters, were investigated. Thus a direct comparison can be made between donor-doped and donor-free points which have been given similar forming pulses. The forming pulses were of the capacitor discharge type, with voltage and RC values similar to those used in conventional transistor forming. The points used were of the cantilever variety, and the n-germanium was zone-leveled material in the 3 to 4 ohm-cm range. Two points were supported in a double-ended micro-manipulator which allowed freedom of movement in 3 dimensions for each point.

2.2.1 *Potential Probes*

Conventionally, point-contact transistors are made on a superoxol-etched wafer. This etch leaves a rough surface which is unsuitable for accurate potential probing. Some measurements were made of the floating potentials on this kind of surface, but accurate results were difficult to obtain. In a later section it is shown that the kind of etch used in surface preparation can have profound effects on the degree of forming obtained. However, it is shown that forming characteristics of an "aged" CP_4-etched surface are quite similar to the superoxol surface. Thus this kind of surface was used, since its topographical uniformity allows very reproducible results in the measurement of floating potentials.

Fig. 2 is a comparison of the floating potentials for the two kinds of transistor points examined. The log-log plot shows the magnitude of the floating potential, V_p, near the reverse biased collector as a function of r, the distance of the probe from the collector measured between centers of the two points. The bars represent the uncertainty in measurement of the linear distance. Three curves are shown. The lowest Curve I represents the potential near a Be-Cu point formed with a conventional forming pulse. Curve II is a plot of the potential near a similarly formed phosphor bronze point, while Curve III represents data obtained using such a point more heavily formed. In all cases the magnitude of the floating potential decreases inversely as the distance from the point, and is given

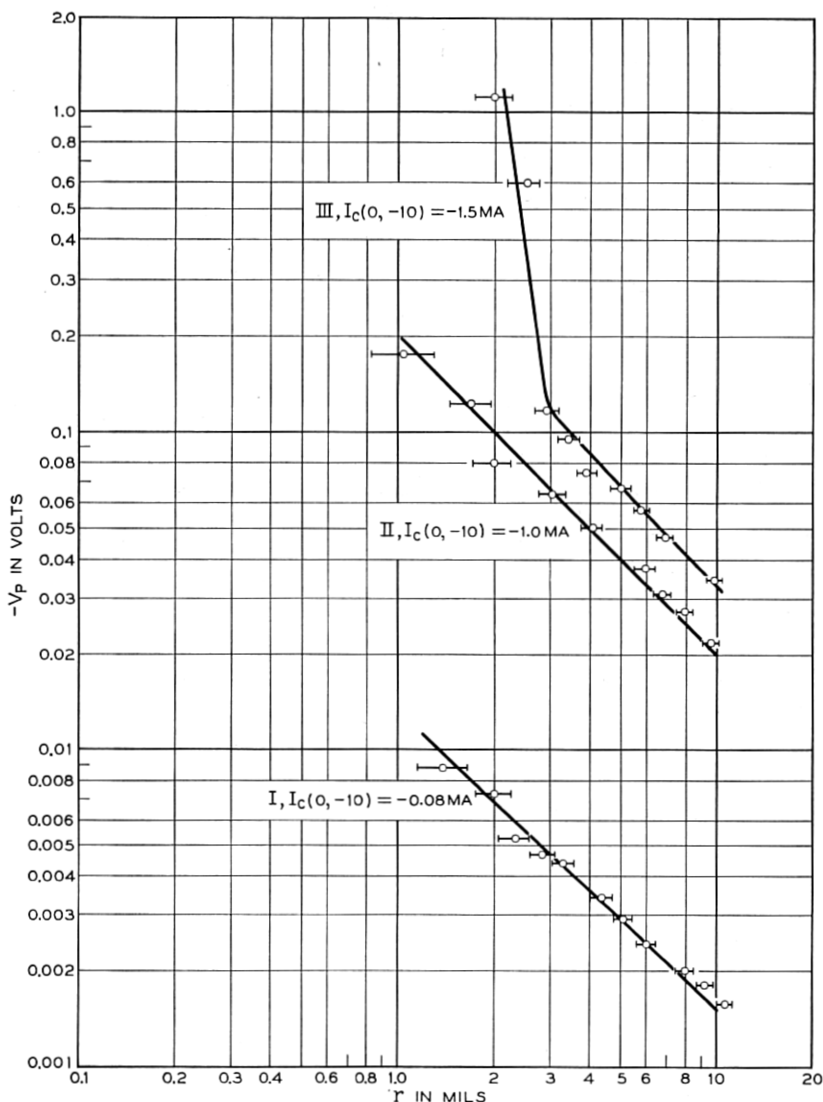

Fig. 2 — Comparison of floating potentials near formed points.

by $\rho I/2\pi r$ where ρ is well within the range of the measured resistivity (3–4 ohm-cm).

Thus the effect of adding the donor to the point wire is to increase the reverse current and increase the floating potential near the point by an order of magnitude. One would therefore expect an accompanying

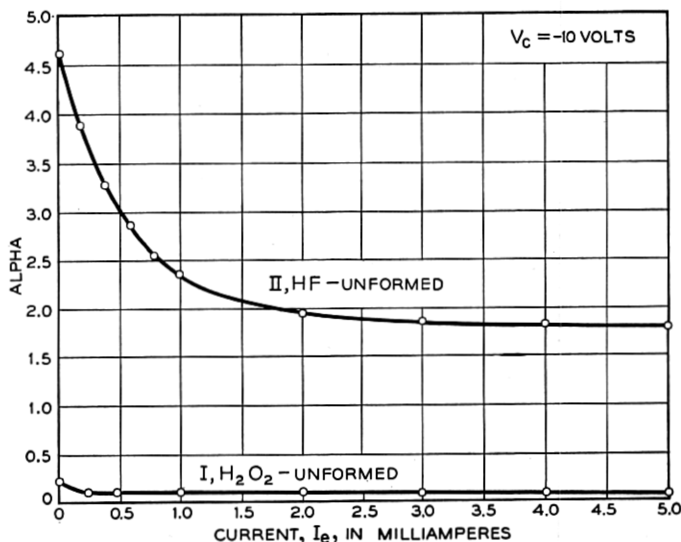

Fig. 3 — Comparison of alpha-emitter-current characteristics of formed points.

increase in the drift field near the point and a corresponding increase in α. Fig. 3 indicates that such is the case. The small signal α is plotted as a function of emitter current in Curves I and II. The point spacing in this case is 2.5 mils. It is interesting to note that the peak at low emitter currents is present in both cases, in spite of the fact that presence of a p-n hook is not likely when the Be-Cu point is formed.

It is thus apparent that the forming the Be-Cu point produces a structure which more closely resembles a p-n junction. The effect of adding the donor is to reduce the resistance of the junction. Further contrast between these two kinds of contacts is demonstrated by comparing forward currents through the contacts and their capacities. In Table I, a summary of all the contrasting properties is given. All values quoted are representative values.

2.2.2 *Use of the Copper Plating Technique*

During the investigation of these contact properties, an interesting way of illustrating their physical properties was developed. This technique, borrowed from junction transistor technology, can be used to identify visually the boundary between the formed region and the bulk germanium in a metallographic section of a point-contact transistor. It further appears that modifications of the technique will enable determination of

TABLE I

Contact	Formed Be Cu	Formed Phosphor Bronze
$I_c(0, -10)$ ma	−0.01 ma	− 1.0 ma
$I_c(6, -5)$ ma	−1.0 ma	−14.0 ma
$I_c(0, +0.5)$ ma	2.8 ma	0.8
Peak value of α	0.25	4.5
α (5.0, −10)	0.1	1.7
Capacity ($Vc = -5V$)	3.0 $\mu\mu$f	$<$ 0.1 $\mu\mu$f

the equipotentials surrounding a collector or emitter point under bias, and visualization of current flow patterns in point contact transistors under bias operating conditions.

Use of this technique in identification of formed transistor properties is quite simple. A transistor container (including only the completed header, wafer, and point-contact structure) is filled with araldite plastic, which is allowed to harden. The collector point is then electrically formed. The plastic is necessary to ensure that the collector point does not subsequently move from the formed area. The can itself is then embedded in a plastic block, which is lapped down to expose a cross section of the unit, Fig. 4(a) and (b). Both the collector point and the base electrode are well masked, Fig. 5. A droplet of $CuSO_4$ solution of fairly low concentration is placed on the germanium, so that it is in physical contact only with with the germanium and the masking plastic. In order to identify the formed region, a reverse bias of 20 volts or so is applied between the collector point and the base contact for a time usually of 0.1 second or less. Actually, best results have been obtained by applying the reverse

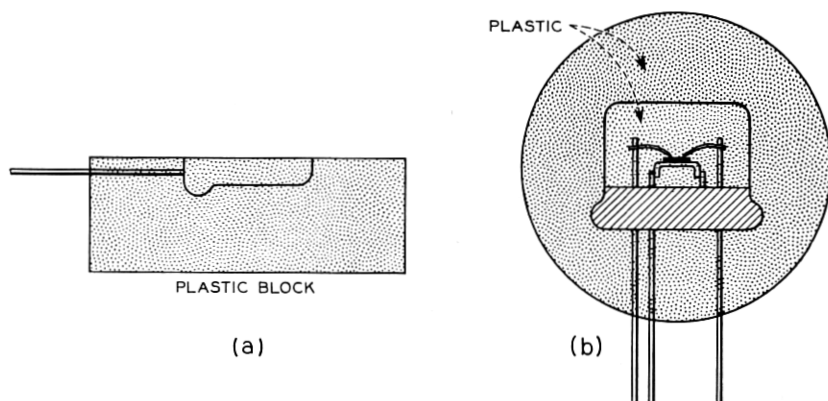

Fig. 4 — Preparation of a transistor for copper plating.

bias in the form of a condenser discharge pulse. Care must be taken to avoid changes in contact characteristics resulting from the plating pulse. The deposit of copper does not appear instantly after pulse application, but may require several seconds before becoming visible. At the instant the deposit becomes visible, the plating solution is washed off.

Fig. 6(a) and 6(b) show the results of the plating operation on a formed collector point and a formed emitter point. Both pulses were similar to, though somewhat "heavier" than those usually used to form transistors. These units were plated under the conditions illustrated in Fig. 5(a). The floating potential in the vicinity of the reversed bias point can be measured as a function of the distance, r, from its center, using an auxiliary tungsten point. Qualitatively this potential is shown as a function of the distance, r, in Fig. 5(b). In this case most of the drop in magnitude of the potential appears within a radius, r, less than 0.002 inches, provided surface conductivity is small. The conductivity of the plating solution is kept small to ensure that the potential distribution in the germanium is not altered by presence of the solution. Under these conditions, it is assumed that, although copper ions in solution are attracted towards the highly negative regions of the germanium, the main current flow is through the germanium, except for regions of high potential gradients. In these regions some of the current will be carried by ions in the solution, by-passing the region. If the formed region boundary is a sharp p-n junction, one would expect a plating pattern as observed in Fig. 6(b) and 6(d), as is observed with the donor-free emitter point. For the more complicated structure produced by forming the

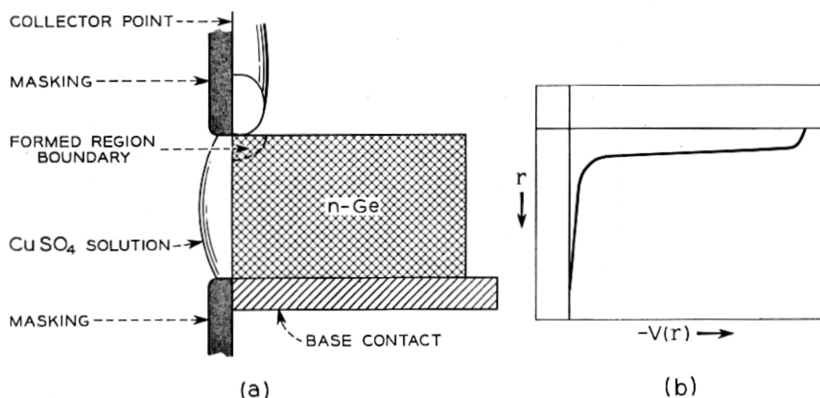

Fig. 5 — Experimental conditions for copper plating.

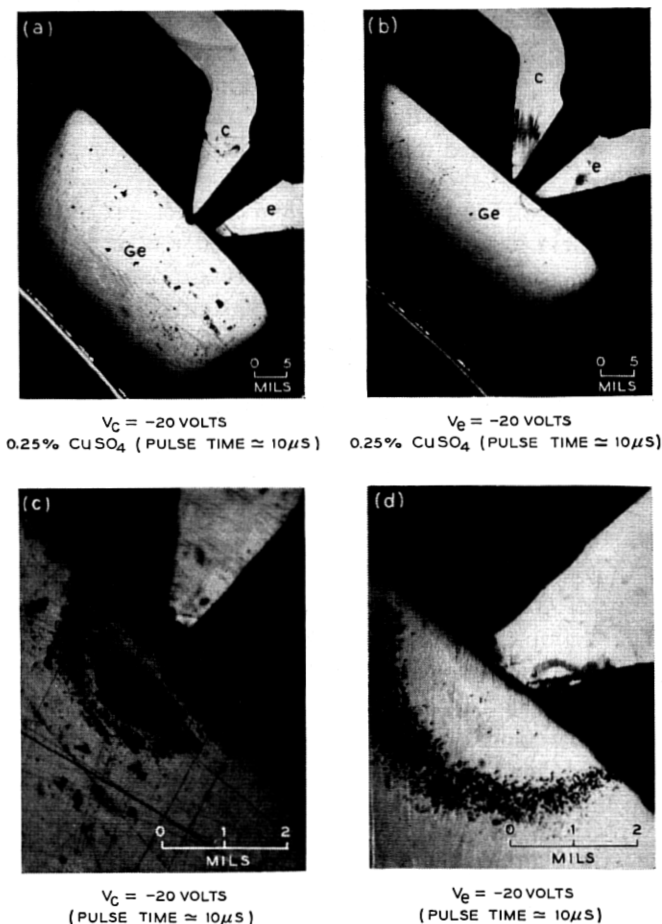

Fig. 6 — Copper plated formed layers in point-contact transistors.

collector, the pattern obtained is more difficult to interpret, Fig. 6(a) and (c). However, in both cases the disturbed areas are roughly comparable in shape and size.

Differences in the forward characteristics of the collector and emitter points may also be graphically observed by means of the plating technique. In Figs. 7(a) and 7(b) are sketches of patterns obtained by applying forward bias to contacts for plating. In this case a more concentrated solution is used, and the plating time is longer. In Fig. 7(a) is shown the pattern obtained when an unformed collector point is biased for-

ward during the plating pulse. The copper deposits to within the order of a diffusion length from the emitter point. Fig. 7(b) shows the pattern obtained by plating the region near a forward biased formed collector. Here again the copper has deposited over practically all of the base wafer surface, except for a much smaller hemispherical region near the collector point.

By adjustment of the plating time and solution concentration, the almost radial field in the bulk germanium under a reverse-biased collector point can be detected. Under similar conditions, an emitter point biased to the same voltage shows a plating pattern similar to that of Fig. 6(b), with little evidence of the radial field. This would be expected from the potential plots shown in Fig. 2.

These techniques serve merely to illustrate graphically the differences in the two types of contact. Although both points when formed give rise to a formed region in the bulk germanium of similar size and shape, the diode characteristics of the junction under the donor-doped point are degraded.

The plating technique may also be adjusted to allow sensitivity to the current flow pattern in a transistor with both points biased to operating values. The example shown in Fig. 8 demonstrates visually the bulk nature of the current flow in the point contact transistor. Here the copper plates out on the negative regions of the crystal and is noticeably absent from the regions of high hole density under the emitter point. In the region to the left of the collector indicated by the arrow, the plating is partially obscured by masking. The size of the copper-free region under the emitter point may be reduced to substantially zero for the same I_e by increasing the bias applied to the collector.

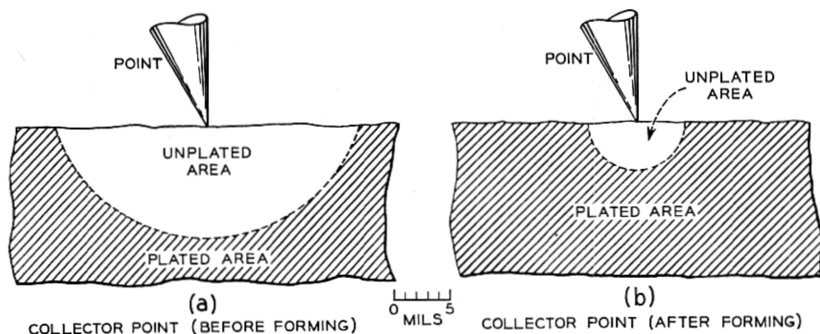

Fig. 7 — The effect of forming and current flow in point-contact collectors.

2.3 *Under-Formed and Over-Formed Contacts*

One of the problems encountered in the large-scale manufacture of point-contact transistors is the variation in the forming yield. Thus, forming to a specified criterion of transistor performance does not always result in a uniform product. Although considerable care may be taken to ensure uniformity of all bulk properties and forming technique, a large variation may be encountered in the output characteristics of the transistors. In Section 4, a prime factor in determining the efficiency of forming is shown to be the chemical history of the germanium surface. Uncontrollable variations in surface conditions may therefore often account for much of the variations in results of a specific forming technique.

Such variations often manifest themselves merely as differences in degree, but may show up as differences in kind, taking the form of anomalous output characteristics. These have been classified by L. E. Miller[14] into three qualitatively different phenomena. The first of these, referred

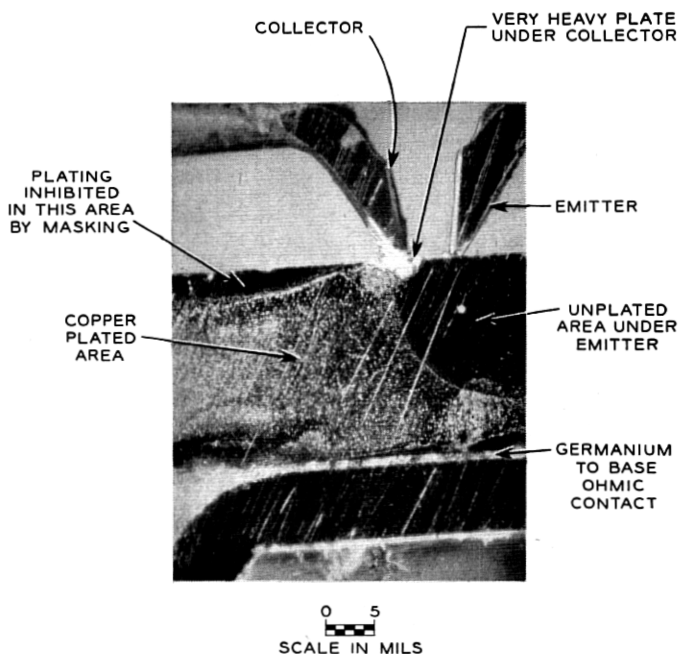

Fig. 8 — Flow geometry for a low alpha point-contact transistor.

to as the type (1) anomaly, is of interest here since it represents a collector contact whose physical properties are between the extremes listed in Section 2.2. Miller has shown that the source of this kind of output characteristic can be identified as the formed area under the collector point.

Essentially this anomaly consists of an abrupt rise in the current gain as the collector voltage V_c is increased at constant emitter current. Beyond the critical value of V_c, the characteristic of the unit resembles that of a well formed transistor. One is led to consider that such a contact is under-formed, in the sense that at low V_c, collection of holes is inadequate. Further support is lent to such a definition by the data of Miller, which shows a definite increase in the occurrence of anomalous units with a decrease in the I_{co} of the contact. Such an increase occurs regardless of whether the I_{co} decrease is obtained by decreasing the donor concentration of the point wire, or by increasing the time constant of the forming pulse. In Table II are compared collector capacity and I_{co} measurements made in units with and without output characteristic anomalies. The capacity of these anomalous collectors also appears to range between the two extremes listed in Table I. Thus there is evidence that these collectors are intermediate between the extremes cited in Table I in the sense that at low reverse biases the drift field is low, and the properties of the formed barrier resemble those of a formed donor-free point.

The results of detailed investigation of the properties of such anomalous characteristics now being conducted will be published at a later date. The present experimental results indicate that the instability occurs when the extra current to the collector, ΔI_c, reaches a critical value. In this respect, increasing the transport factor β, by increasing V_c, or increasing the emitter current are equivalent. At a roughly critical ΔI_c, the transition between a low α and a higher value of α occurs. After the transition, the unit behaves like a conventional point contact transistor, with a current multiplication on the order of $(1 + b)$ at higher values of I_e. Thus the origin of this kind of anomaly may lie in the lowering of the formed barrier by the space charge of the holes, a mechanism suggested by Bardeen.[15]

TABLE II

	$I_c(I_e = 0, V_c = -10$ volts$)$	$C_c(I_e = 0, V_c = -10$ volts$)$
Typical Transistor	1.0 ma	0.1 $\mu\mu$f
Typical Anomalous Transistor	0.2 ma	0.5 $\mu\mu$f

The other anomalous collector characteristics considered by Miller have their origin in the relation between the transport factor and the properties of the emitter at various operating conditions. In view of the relations existing between the occurrence of these anomalies and the I_{co} of the collector contact, there is some justification for classification of these contacts as "over-formed."

3. PROPERTIES OF UNFORMED POINT CONTACTS

3.1 *Physical Properties of Metal-Semiconductor Contacts*

The classical ideas on the nature of the rectifying metal-semiconductor contact have undergone substantial revision since the consideration by Bardeen[16] of the importance of surface states and the work on the point contact transistory by Bardeen and Brattain. According to Bardeen's model, the nature of the space charge layer at such a contact is to be considered largely independent of the metal used for contact, and is primarily dependent on the charge residing in localized states at the germanium surface. Thus the rectifying properties of the metal semiconductor contact in air are expected to be largely independent of the work function of the contact metal.

The question of the exact nature of the surface charges is not yet readily answerable. Charges may arise which consist of electrons and holes residing in surface states of the type proposed by Tamm.[17] On the other hand, other surface charges may arise as a result of adsorbed impurity ions, or from adsorbed atoms or molecules having electrical dipole moments. Brattain and Bardeen[18] have shown that the space charge layer is dependent on the surrounding ambient and have indicated that charge may reside on the outer surface of a film (presumably an oxide layer) at the germanium surface as well as in surface states of the type mentioned above, which are presumably those responsible for surface recombination processes.

Thus, it is the surface charge on the semiconductor, rather than the nature of the metal, which primarily determines the nature of the potential barrier which exists at a metal semiconductor junction.

A schematic electron energy diagram for the contact between a metal and an n-type semiconductor is shown in Fig. 9. The potential barrier φ_0, and the nature of the space charge layer in the semiconductor are determined by the surface charge system and the bulk properties of the semiconductor. In turn, the surface charge system is dependent upon such factors as the ambient at the germanium surface and the chemical history of the surface.

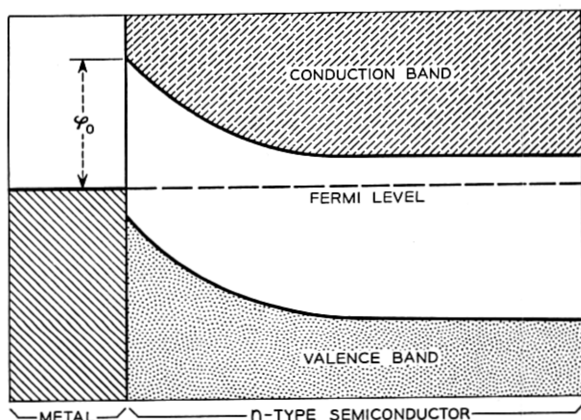

Fig. 9 — Electron energy diagram for a metal-semiconductor contact.

The experiments of Brown[19] indicate that the presence of charge on the surface of *p*-germanium can alter the space charge in the crystal near its surface and, in some cases, produces an inversion layer of *n*-germanium at the surface. Garrett and Brattain[20] have shown that a change of ambient from sparked oxygen to dry oxygen to wet oxygen can increase I_{co} and floating potential on n-p-n junction transistors, and the process is reversible. Their interpretation is that sparked oxygen builds up a film, presumably germanium oxide. Oxygen atoms on the surface, negatively charged, can give rise to a p-type inversion layeı on n-germanium. Moisture apparently counteracts this negative charge, and humid oxygen can cause an n-type inversion layer on p-germanium, which can be removed with a dry oxygen ambient.

Thus, the electrical resistance of an unformed metal-germanium contact on an etched germanium surface can be expected to be extremely sensitive to any chemical treatment which tends to affect the constitution of the oxide layer present on the surface, regardless of the metal used for contact in air. Bardeen and Brattain,[1] in early transistor experiments, have shown that such is the case. They have used transistor collector points on germanium surfaces which, after etching, were subjected to an oxidation treatment (heating in air).

In this section are described experiments which seem to indicate that the reverse resistance of unformed diodes on etched n-germanium surfaces can be decreased by chemical surface treatment, and the magnitude of the floating potential near such contacts is increased to sufficient extent that the point can serve as a multiplying collector. Average α for

these points approaches values found in electrically formed collectors. Subsequent parts of this section will be concerned with description of the experiments involved and comparison of the electrical characteristics of these points with those of conventionally formed points.

The effections of electrical forming on donor-doped and donor-free point contacts have been described in earlier sections. It has been stressed that the addition of the donor element to the point results in a contact with degraded diode characteristics, but which serves as an excellent collector.

The possibility of an analogous situation in an *unformed* point collector exists, with the electrical forming of the donor-doped point being replaced by a suitable chemical treatment of the surface. The experiments described below indicate that such is the case.

3.2 *Experimental Procedures*

The germanium used in these experiments was zone-leveled material. The n-germanium was in the 3 to 4 Ω-cm range. Originally, experiments were run using slices, about 0.025″ in thickness, soldered on flat brass blocks, with the brass well masked with polystyrene. Germanium dice, already mounted on standard base-header assemblies used in a hermetic-seal transistor process pilot line, were also used.

The ground surface of a slice was given a three-minute chemical etch (CP_4 or superoxol), washed in pure water (conductivity <0.1 micromho), and blown dry in a nitrogen stream. This surface could then be exposed for several minutes to 24 per cent HF, hot zinc chloride-ammonium chloride solder flux, or other chemical treatments as the experiment might require. These solutions were applied to the slice or die in the form of large droplets, so the solution did not come in contact even with the masking. Later, in order to make doubly sure that contamination from the base or base contact was not involved, all experiments were repeated using a two-inch length of a zone leveled bar with a base contact soldered on one end, and the other end, freshly ground between treatments, used as the surface under examination. The etching was done by lowering one end of the bar about one-half inch into the etch, leaving the contact end a good distance from the etch. The etched surface could subsequently be exposed to any desired chemical treatment. After the chemical treatment, the sample surface was again washed in low conductivity water for several minutes and blown dry with nitrogen.

The sample, after chemical treatment, was placed on a double ended manipulator base, used to control the position and pressure of two canti-

lever points on the treated surface. The electrical characteristics of a beryllium copper point, operating as transistor collector on the treated surface, could then be investigated. An auxiliary etched tungsten point doubled as a potential probe and as an emitter. A switching arrangement allowed oscilloscope presentation of the I_c-V_c collector family and the alpha-emitter current sweep, measurement of the emitter floating potential on a high impedance VTVM, and determination of other transistor parameters for any desired position of the emitter point.

Phosphor bronze collector points were not used since it was found that, on certain chemically etched surfaces the mere application of a negative bias of 15–40 volts for a few seconds sometimes is sufficient to cause electrical forming of the point in the sense that I_{co} and average α are increased by an appreciable amount.

The beryllium copper points were carefully cleaned to prevent contamination by donor elements. Their cleanliness was then tested by other methods described in Section 3.3.6.

With this arrangement, most of the electrical properties of a given manipulator unit could be inspected during the time the unit "survived." These electrical measurements were made in room air (R. H. between 20 and 30 per cent), although provision was made for directing a continuous stream of dry nitrogen at the points and surrounding surface.

3.3 *Experimental Results*

3.3.1 *Unformed Transistors on Superoxol Etched* Surfaces*

A striking difference was observed in the electrical characteristics of unformed collector points on the various n-germanium surfaces examined. In particular, surprisingly large values of $I_c(0, -10)$ and $I_c(6, -5)$, (the latter taken as a measure of average α), were encountered on the superoxol etched surface subsequently "soaked" for about 10 minutes with 24 per cent HF. At these locations the unformed transistor action was quite similar to that observed with a conventional phosphor bronze point formed on a freshly etched surface.

These large values were found only in specific locations on the treated surface, there being a random fluctuation of $I_c(0 -10)$ and $I_c(6, -5)$ with location of the points on the surface. However, no such large values of these parameters were found (together) on surfaces freshly etched in superoxol. The α as a function of emitter current for the unformed points (2.5 mil spacing) on a superoxol etched surface, before (Curve I) and after (Curve II) HF treatment is shown in Fig. 10. Comparison with

* One part 30 per cent H_2O_2, one part 48 per cent HF and four parts water.

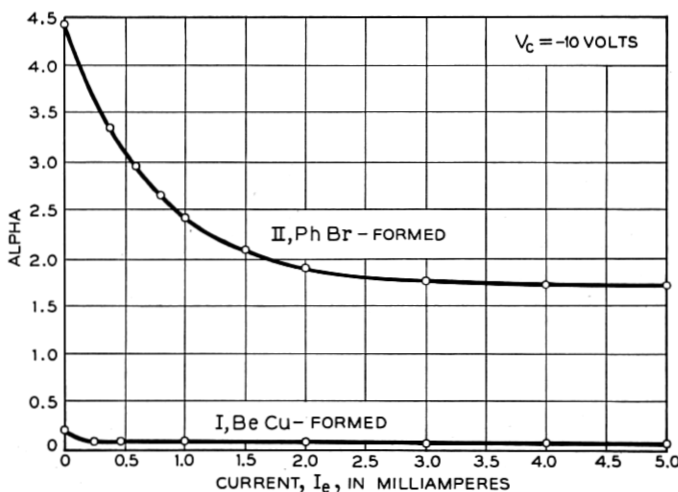

Fig. 10 — Comparison of alpha-emitter-current characteristics for unformed collectors.

Curve II, Fig. 3, indicates that the $\alpha(I\varepsilon)$, obtained after the HF treatment, is comparable to that of a phosphor bronze collector formed conventionally on the same etched surface before treatment. (It turns out that conventional electrical forming on the etched surface after the HF treatment is more difficult, and in cases as referred to above, where the α is not initially high, requires an excessive number of pulses to bring the α to a normal value.)

In Table III are listed the maximum and minimum values of some transistor parameters found on the same superoxol-etched surface before and after the HF treatment (point spacing about 2 mils).

It is seen that the effect of the subsequent HF treatment after the superoxol etch is at least in some locations on the treated surface to increase the $I_c(0, -10)$ and the average α, in some cases to values approaching those encountered in conventionally formed point-contact transistors. There is also a lowering of the forward current of the unformed collector point after the HF treatment. It is not to be implied from this table that the I_{co} is always found to be low on fresh superoxol-etched surfaces. Actually high values of $I_c(0, -10)$ have been occasionally found on surfaces freshly etched in superoxol. However, these collectors seldom have high values of average α, and it is suspected that here the higher reverse current is associated with excessive surface conductivity. Treatment of such a surface with HF always serves to increase the average α, and decrease the forward emitter current, with

Table III

Parameter	After 3 Min. Superoxol Etch		After Subsequent 10 Min. "Soak" in 24% HF	
	Max. Value Observed	Min. Value Observed	Max. Value Observed	Min. Value Observed
$I_c(0, -10)$ ma	−0.16	−0.06	− 0.98	−0.20
$I_c(6, -5)$ ma	−7.0	−0.95	−13.5	−7.0
$I_c(0, +0.5)$ ma	2.8	2.0	2.3	1.3
Peak value of α	3.0	0.15	6.0	2.0
α (5.0, −10)	0.50	0.09	2.0	0.5

no significant changes in the extreme values of $I_c(0, -10)$ encountered initially. Some of the unformed units have collector families quite similar to those of an electrically formed point-contact transistor. However, the resemblance ends when stability of operation is considered. When the unformed units are operated in room ambient, hysteresis loops are occasionally observed, either in the I_c-V_c output characteristic sweep, or the α-emitter current sweep. This hysteresis can be eliminated by directing a stream of dry nitrogen across the germanium surface in the vicinity of the points. It is not known whether the hysteresis is thermal or electrolytic in nature. The operation of these unformed units, even in the absence of hysteresis, is extremely erratic and unstable. Operating a unit at a high power level will cause loss of α and I_{co}, and mechanical shock delivered to the collector point while the unit operates under bias may cause loss or gain of α and I_{co}. In cases where I_{co} (and α) are low when the collector point is initially set down on the treated surface, an increase in I_{co} and α may be brought about by mechanical motion of the point, (such as "tapping" the manipulator base, or dragging the point across the surface). In other cases the high α and I_{co} are found immediately after the point is set down on the freshly treated surface, without any such procedure. None of these effects is observed to an appreciable degree on a freshly etched surface without further treatment.

The effect of zinc chloride-ammonium chloride solder flux on fresh superoxol-etched surfaces was also investigated. In this case, after the etch, the surface was immersed in almost boiling solder flux for about ten minutes. The effect of this surface treatment on the performance of the unformed transistors was entirely similar to the results quoted in connection with the HF treatment. The treatment increased the reverse collector current and average α, and decreased the forward collector current, on the average. Magnitudes of $I_c(6, -5)$ as high as 14 ma were observed on surfaces treated in this way.

3.3.2 *Unformed Transistors on CP_4-Etched Surfaces*

With reference to unformed point contact properties, the CP_4-etched surface is not at all similar to the superoxol etched surface. If two beryllium-copper points are put down on a ground surface freshly etched in CP_4, and operated as a transistor, high values of $I_c(0, -10)$ and $I_c(6, -5)$ are often encountered. However, after an hour or so in room air, both these parameters decrease and after an overnight exposure to room air, the properties of the surface with regard to the transistor action resemble those of a surface freshly etched in superoxol. At this point, a treatment in 24 per cent HF will return $I_c(0, -10)$ and $I_c(6, -5)$ to their originally high values. These effects are summarized in Table IV.

3.3.3 *Diode Characteristics on Electro-Etched Surfaces*

It has been found that the rectification properties of unformed point diodes may also be changed conveniently by changing the conditions during an electrolytic etch in KOH solution. These results are summarized in Table V which represents typical variation in reverse current, I_r, with surface variation attainable by adjusting the current density and etching time. In each case the measurements represent data taken on germanium cut from adjacent sections of the same ingot and given the surface treatment noted in the table. In general the electro-etched and chemically etched results agree; that is, any treatment which appears most likely to leave an oxide film (such as the use of a high current density during electro-etching) will yield a diode with improved rectification characteristics.

3.3.4 *Output Characteristic Anomalies*

In the process of examining these chemically treated surfaces, some of the superoxol-etched n-germanium surfaces were given additional

TABLE IV

Parameter	Value after 3 Min. CP_4 Etch		Value after 16 Hrs. in Room Air		Value after 10 Min. in 24% HF	
	Max. Value Observed	Min. Value Observed	Max. Value Observed	Min. Value Observed	Max.	Min.
$I_c(0, -10)$ ma.	−1.7	−0.30	−0.10	−0.04	−1.0	−0.06
$I_c(6, -5)$ ma.	−13.3	−11.0	−7.0	−2.0	−17.5	−8.0
Peak value of α	4.5	2.5	2.0	0.75	9.0	3.0
$\alpha(5.0, -10)$	1.8	1.0	1.0	0.25	2.0	0.75

TABLE V

Etch Treatment in 0.1% KOH	I_r (−10 volts)
10 ma for 30 sec	−0.16 ma
5 ma for 30 sec	−0.37
2.5 ma for 30 sec	−0.55
5 ma for 1 min	−0.04
2.5 ma for 1 min	−0.18
1.75 ma for 1 min	−0.74

treatments in H_2O_2 (superoxol strength). In general, no great differences were observed in the unformed alpha and $I_c(0, -10)$ after the treatment. However, in isolated cases, unformed units made on etched p-germanium treated in this way exhibit output characteristic anomalies of the type characterized by Miller as type (1). It was later found that the same surface treatment can produce a similar result on etched n-germanium surfaces, again only in isolated locations on the surface. An output characteristic of this form is shown in Fig. 11. This unformed unit was made on a superoxol-etched n-germanium surface with a subsequent three-minute soak in H_2O_2. This characteristic was extremely sensitive to variation in point pressure.

Miller has also referred to output anomalies of types (2) and (3), which are usually associated with close point spacing in conventional point-contact transistors. Such types of anomaly have been observed in unformed units (with high average alpha) made on HF treated surfaces.

3.3.5 *Floating Potential Measurements*

In all cases where the $I_c(0, -10)$ and average alpha on etched surfaces are increased by the HF or solder flux treatment, these increases are accompanied by an increase in the magnitude of the floating potential near the reverse-biased collector. In Fig. 12 the magnitude of the floating potential V_p of a sharp tungsten probe near the reverse-biased collector is shown as a function of r, the distance of the probe from the collector (r is approximately the distance between the center of the two point contacts). The surface used in this experiment was prepared by chemical polish for three minutes in CP_4 and subsequent storing in room air for sixteen hours. This provided a smooth surface which resembled, at least with regard to electrical characteristics, a freshly etched superoxol surface.

Curve I represents the potential-distance plot for an unformed BeCu point on the aged superoxol-etched surface. Curve II represents a similar plot for an unformed BeCu point taken after the surface was given a ten-minute soak in 24 per cent HF.

The measured resistivity of the germanium used in this experiment was 3.3 to 3.6 Ω-cm. It can be seen from Curves I and II that increase in the magnitude of the floating potential near the unformed point on the etched surface after the HF treatment is, to a rough extent, proportional to the increase in $I_c(0, -10)$ produced by the treatment. Values of $2\pi V_p r/I$ taken from lines of slope (-1) drawn for best fit through points on the individual curves give reasonable agreement with the measured resistivity. For curve I, $2\pi V_p r/I = 3.3$ ohm-cm, and for Curve II, $2\pi V_p r/I = 3.5$ ohm-cm.

By comparing Curves I and II of Fig. 2 with Curves I and II of Fig. 12, it can be seen that the effect of treating the surface under the unformed point with HF is analogous to adding donor to the formed point

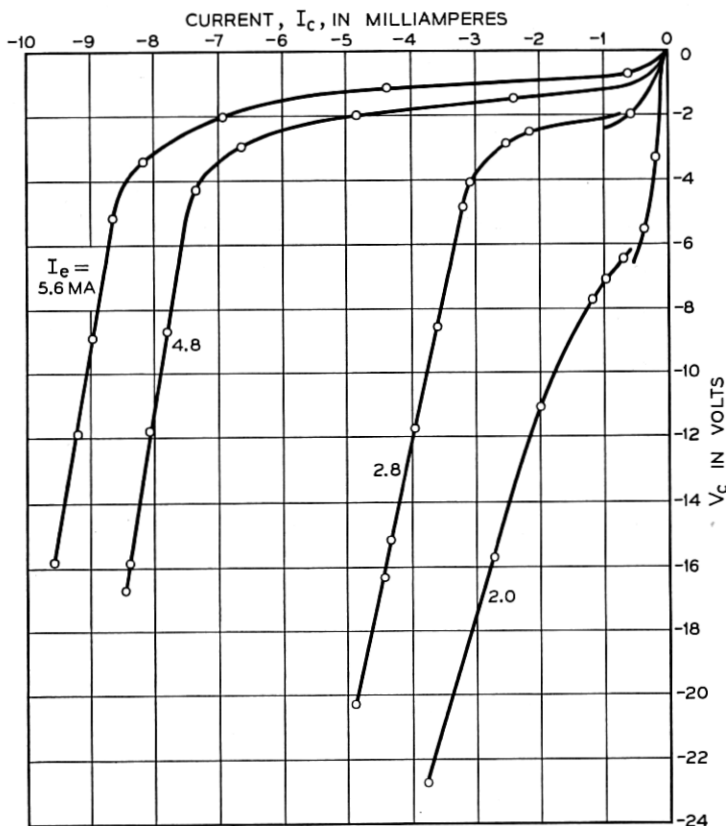

Fig. 11 — Type (1) collector anomaly observed in unformed unit (n-type germanium).

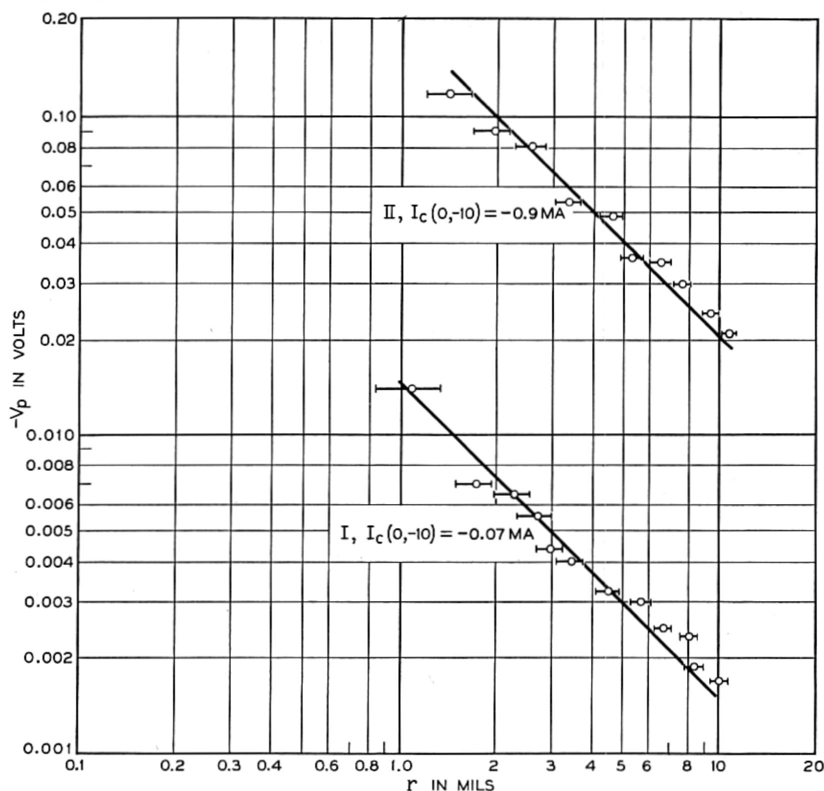

Fig. 12 — Comparison of floating potentials for unformed point-contact collectors.

on the etched surface. It seems reasonable to ascribe the increased negative floating potential after the HF treatment to an increase in current density through the surface under the point, rather than to any increase in surface conductivity. It is worth noting that on superoxol-etched surfaces, the negative floating potential near an unformed collector point can often be increased by an order of magnitude by blowing a stream of dry nitrogen near the point. This effect may possibly be a result of excess surface conductivity, but in these cases is *not* accompanied by any appreciable changes in $I_c(0, -10)$ or average alpha.

3.3.6 *Contamination of Collector Points and Surfaces*

Past experience with use of point-contacts as transistor collectors indicates that experiments may often be confused or confounded by unsus-

pected contamination of the points used. For this reason, particular attention was given to chemical processing of the beryllium copper points used in the preceding experiments. These points were chemically cleaned to remove oxides and unwanted contaminants, and carefully washed before use. Several lots were processed at different times, and all experiments repeated on the different lots, with no contradictory results.

It is particularly important that the point be free from donor elements, since it has been observed that that phosphor bronze points or "poisoned" beryllium copper points washed with a lithium chloride solution often exhibit on superoxol etched surfaces a kind of "forming" after the application of reverse bias. The symptoms of this are a sudden increase in I_{co} which take place as the reverse bias is increased above 15–20 volts. The alpha emitter current sweep shows evidence of excessive noise in such a case, and it is not until the collector is given a conventional forming pulse that this excessive noise is eliminated, and the unit becomes stable in operation.

A donorless point can be reasonably identified by the fact that electrical pulsing, heavy or light, will not increase the initially low average alpha on a superoxol-etched surface to values much above 1.0, although I_{co} may be increased or decreased depending on the type of condenser discharge used. The beryllium copper points used were tested on superoxol-etched surface to make sure they showed no tendency to form electrically.

If high values of alpha can be found when these points are used as unformed collectors on the surfaces treated in HF or solder flux, the question arises whether such values may be attributable to presence of a donor element left on the surface in some mysterious way by the chemical treatment. If such is the case, the donor might, at high enough reverse bias, be responsible for an increased alpha in a manner similar to that observed in connection with the forming in under bias of phosphor bronze collectors on etched surfaces. Two precautions were taken in this connection. No reverse bias greater than 10 volts was ever applied intentionally to these collectors during experiments (with exception of the unit in Figure 11), and secondly, forming characteristics of both phosphor bronze points and the beryllium copper points on this type of surface were investigated.

It was found that on a superoxol surface treated with HF or the solder flux, a phosphor bronze point would form to a high average α, but this invariably required more forming pulses than on a superoxol etched surface. "One-shot" forming is common for a superoxol etched surface, whereas after the HF or solder-flux treatment, forming to high average

TABLE VI

	Point			
	Beryllium Copper Collector		Phosphor Bronze Collector	
	Occasion			
	Before Forming	After Four Forming Pulses	Before Forming	After Four Forming Pulses
$I_c(0, -10)$..........	−0.75	−0.50	−0.80	−2.5
$\alpha(5.0, -10)$........	1.5	0	1.5	2.0
Noisy..............	Yes	Yes	Yes	No

alpha invariably requires at least three and sometimes many more "shots", although it can be done. This type of formed unit does not exhibit excessive noise in the α-I_ϵ sweeping gear. However, pulsing of the beryllium copper points on the latter kind of surface, in similar fashion, invariably results in loss of alpha and never eliminates the excessive noise. Initially, the pulsing decreases the I_{co} magnitude, but continued pulsing will eventually cause large increases in this case. These results provide circumstantial evidence, at least, that the treated surface and the point are operationally free of any donor element and that the transistor collector barrier involved is at the germanium surface. For example, in Table VI are given some typical data obtained during pulsing of points on a superoxol-etched surface after treatment with near boiling zinc chloride-ammonium chloride solder-flux. A tungsten emitter was used.*

3.4 *Discussion of Experimental Results*

3.4.1 *Effects of the Chemical Treatment on the Superoxol-Etched Surfaces*

It might be presumed that an inversion layer and a relatively high surface conductivity is responsible for the increase in negative floating potential and reverse current observed on the superoxol-etched n-germanium surface after the HF treatment. On the other hand, if it be assumed that at the etched surface, in room air, an inversion layer exists which does not introduce excessive surface conductivity, one can say that the effect of the HF treatment is merely to raise the surface potential, (i.e., to reduce the barrier height for electrons). This might

* Alpha values are usually lower in any given situation when the conventional chisel-type beryllium copper emitter point is replaced by an etched tungsten point.

account for the increase in reverse current density* and a proportional increase in the magnitude of the floating potential near the point. In this case the geometry of current flow across the contact should remain relatively unchanged as indicated by the floating potential measurements. In this way the effect of the HF treatment is somewhat analogous to the addition of a small donor concentration near the surface to counteract the inversion layer. Since soluble oxide layers[21] have been identified on etched germanium surfaces, it is not unlikely that HF (known to dissolve germanium oxide)[22] might act to reduce the effective thickness of an oxide layer. Such a hypothesis is in agreement with the results of other experimenters,[23] who have attributed a surface inversion layer under the point of an n-germanium rectifier to the presence of germanium oxide. They have presumed the oxide is essential to the formation of a good point contact rectifier. The fact that, for a given ambient, the surface potential is determined by the oxide layer thickness has been postulated by Kingston.[24]

3.4.2 *CP_4-Etched Surfaces*

Sullivan,[25] in connection with an experimental investigation of humidity stability of electrolytically-etched and chemically-etched p-n grown junction diodes, shows that CP_4 chemically-etched surfaces become more stable with respect to humidity variation after humidity exposure and cycling at room temperature. Referring to the fact that electron diffraction studies fail to reveal a crystalline oxide film on CP_4 chemically-polished surfaces and to the results of Law,[26] which indicate that oxide films may be formed slowly at room temperature on exposure to water vapors, he attributes the changes of stability on the CP_4 polished surface to the building up of an oxide film. If such a change can take place on the CP_4 chemically-polished surface on exposure to humid room air, then the results of Section 3.3 can be understood under the assumption that the action of the HF treatment is to remove the oxide film.

After the chemical polish, values of $I_c(0, -10)$ and average alpha for the unformed units are high, as might be expected if the polishing operation leaves the germanium surface with no appreciable oxide film. As the oxide film builds up on continued exposure to room air, both of these parameters are reduced. The subsequent application of HF tends to restore these parameters to their original values by removal of some of this oxide film. Thus, the results of this section are in accord with the

* Evidence for an increase in surface recombination velocity on HF treated surfaces is given in Section 4.2.3.

hypothesis discussed in the previous section to account for the effect of HF on the unformed transistors.

Such evidence, however, is at best only indirect evidence for the build-up of an oxide layer on prolonged exposure to room air. In experiments with grown p-n junction diodes, the authors have found great variations in the length of time required for the electrical properties of the diodes to recover after short wash periods in low conductivity water. Thus the slow changes mentioned above may at this point result from simply a longer time required for the surface to "dry out" after the washing treatment. However, a substantial difference in the physical properties of the oxide layer left by the two etches concerned is still implied. In this connection it is also worth noting that hysteresis effects appear primarily in unformed units made on HF treated surfaces.

The results of these experiments have important implications in the technology of point contact transistors. The results of an application of these results to transistor forming procedures are given in the following section.

4. RELATION OF GERMANIUM SURFACE PROPERTIES TO TRANSISTOR FORMING

4.1 *Pilot Production Problems*

The pilot production and early manufacturing stages of cartridge-type point-contact transistors has generally been characterized by periods during which the forming yields have been very high and similar periods of very low yield. Often these alternate periods occurred during the use of germanium taken from the same rod-grown or zone-leveled crystal. Considerable effort has been expended in attempting to correlate these variations in yield to variations, from crystal to crystal, or in different portions of the same crystal, or such bulk properties as resistivity or minority carrier lifetime. Although these properties of germanium do have some effect on device parameters such as average alpha, reverse emitter current, and I_{co}, there has not been any positive indication that variations in yield are attributable to the amount of variation of bulk properties normally found in the germanium which meets the specifications of the particular device concerned.

This problem was compounded during the early stages of the development of the process for hermetically sealing the point-contact transistor. It was found that although reasonable yields were obtained in the cartridge process, equivalent transistors in the hermetically sealed structure were made only with greatly reduced yield. Further, although micro-

manipulator units could be made with no difficulty, the same material fabricated into a completed structure showed completely different characteristics. In the course of investigation of this problem, it was ofund that the nature of the germanium surface treatment and specifically treatments calculated to produce or react with germanium oxide can profoundly affect the "formability" of the germanium surface as well as a number of other transistor parameters in the fabricated units.

It is the purpose of this section to emphasize the importance of considering the surface properties of germanium in attempting to solve such specific problems of development encountered in devices of this type. In particular, the striking variability of transistor forming on etched germanium surfaces subjected to varying chemical treatments and ambients will be described, as well as the effects of such pre-forming treatments on the parameters of the finished units. The experiments discussed in the previous section indicate how changes in the double layer at the germanium surface can influence the characteristics of an unformed point diode. In turn, the experiments below indicate how the characteristics of the unformed diode are related to the device properties of the transistor collector produced by forming the diode.

4.2 *Experimental Results*

4.2.1 *Pilot Process Forming Yields*

The forming yield of a point-contact transistor is determined by the values of the acceptance criteria and the allowable limits for each of these. Often, different criteria as well as different forming techniques are used for different transistors, so that direct comparison of results is quite complex. There are, however, certain common requirements placed on all point-contact transistors:

(a) The unit is formed so that the average alpha is roughly two or more. The collector current at a relatively high emitter current and low collector voltage is usually an approximate measure of this value, $I_c(6, -5)$ for example.

(b) The collector current with no emitter current flowing should be as low as is commensurate with the first objective.

The other transistor parameters are either directly or indirectly related to these. The number of pulses required to achieve the minimum forming objective, therefore, is one direct measure of the formability of a particular transistor; the average alpha obtained after pulsing is another. However, one must consider both average alpha and I_{co}, since while forming to a given average alpha, the I_{co} may increase prohibi-

TABLE VIII

Treatment	No. of Pulses to Form	Average $I_c(6, -5)$	Average $I_c(0, -20)$	Figure of Merit $I_c(6, -5)/I_c(0, -20)$
3 min. in normal superoxol etch	2	−15.5 ma	−0.69 ma	22.4
1 min. in 48% HF	4	−10.2	−3.2	3.2
1 min. in 30% H_2O_2	1	−17.7	−1.9	9.3

oxides which are present so that a good solder joint may be made. Since the oxide on chemically-etched germanium is likely of the soluble form, one might assume that the results of Table VII imply that the action of the flux and heat tends to dissolve or remove this layer. Also implied by the data is that the presence of such an oxide layer is essential to efficient forming.

The experiments summarized in Table VIII further substantiate this hypothesis. These data represent manipulator transistors made on the *same* germanium wafers which had been treated in succession to a normal superoxol etch, a treatment in 48 per cent hydrofluoric acid, and a treatment in hydrogen peroxide, superoxol strength. Since the soluble form of germanium dioxide is known to react with hydrofluoric acid,[22] it is presumed that the action of the HF is to partially or wholly remove any oxide left by the etch. The H_2O_2 tends to restore the original surface conditions left by the etch. Each figure represents the average of five transistors formed to the 2N21 acceptance criterion, ($V_c(3, -5.5) \leqq 2.0$ volts).

In this case the hydrogen peroxide treated units have an extremely high average alpha, but the I_{co} is also higher than for normally etched units. In terms of the device properties, a unit with a more or less typical average alpha with a low I_{co} is more desirable than the one with an extremely high average alpha but accompanying high I_{co}. It has not been determined whether the I_{co} would be lower for the superoxol treated units if it had been possible to form to the same average alpha as the normally etched units. This is an important piece of device design information which is currently under investigation.

It is clear from these experiments that the nature of the germanium surface, and most probably the nature of the germanium oxide layer on it, to a large extent, determines the properties of the transistor formed on this surface. Direct application of this knowledge to the fabrication process of the hermetically sealed point contact transistor has been carried out by N. P. Burcham.

4.2.2 *Relation of Unformed Diode Characteristics to Transistor "Formability"*

From the results of the previous sections, it appears that superoxol-etched germanium surfaces treated with reagents in which germanium dioxide is soluble provide point contact diode characteristics unsuited to electrical pulse forming. Part of this difficulty, manifested in the inability to reach a specified value of average α without a prohibitive increase in I_{co}, probably results from a lower injection efficiency, γ, for the emitter on such a surface. This seems reasonable in view of the lower forward and higher reverse currents indicated in Table III produced by an HF soak. In Section 4.2.3 evidence will be shown that surface recombination is greater on n-type germanium surfaces treated with HF. This effect can also lead to difficulty in forming to high α without increase in I_{co}, since, for the same drift field, one would expect more minority carriers to die at the surface during their transit to the collector.

On the other hand, there is evidence for believing that the nature of the forming process itself may be quite different on an HF treated surface. Fig. 14(a) shows the time dependence of the collector voltage during a typical condenser discharge forming pulse.

The envelope of the voltage pulse follows roughly an exponential decay of a condenser-resistor series combination. However, inspection shows that during the discharge time, the resistance of the combination

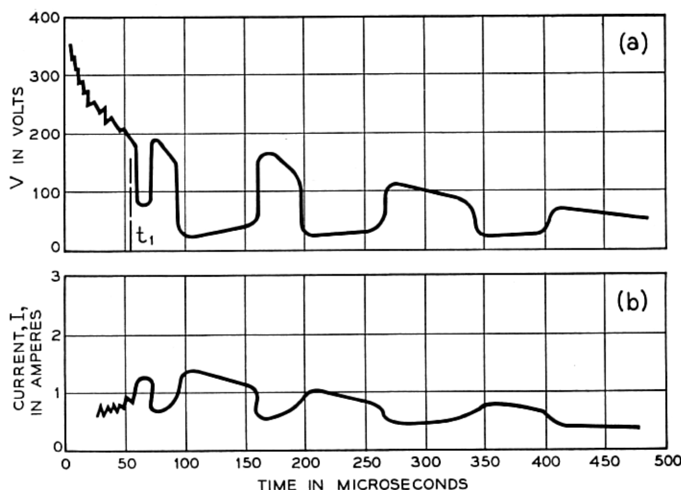

Fig. 14 — Collector current and voltage versus time for a condenser discharge forming pulse.

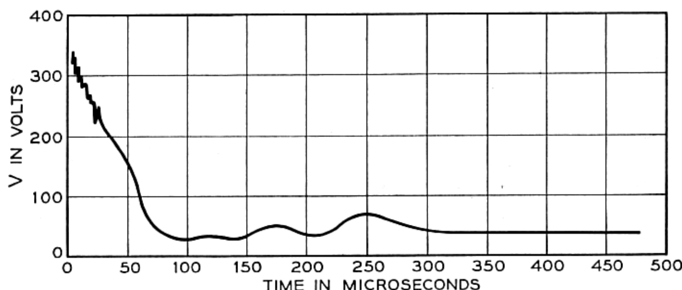

Fig. 15 — Forming voltage pulse for HF treated surface.

undergoes a succession of breakdown and recovery intervals. In Fig. 14(b) is the accompanying plot of current against time. Comparison of these two plots shows that following the application of the voltage, the resistance of the contact decreases until a rather sudden more rapid decrease in resistance occurs, taking place at time t_1. In view of this time scale, the first decrease can be attributed to a heating of the contact, a form of thermal breakdown at the metal-semiconductor surface.[27] Any reason invoked to account for the second more rapid decrease in resistance must account for the short time (a few μs) in which this change occurs. In any event, shortly after the second "breakdown," a quenching results, with the collector resistance returning to a value nearer to its original value. This sequence of events is roughly repeated until the condenser is discharged.

The properties of the contact at nominal reverse voltage and currents are usually changed as soon as one such condenser discharge pulse has occurred, and often one such pulse is sufficient to reach the forming objective. A typical forming pulse obtained under similar conditions to those for Fig. 14 is shown in Fig. 15, with the exception that the surface has been treated in HF for a few minutes. On this case it is apparent that the second, rapid breakdown is entirely absent. The well-defined forming pulse of Fig. 14 is usually obtained on surfaces with good pre-forming diode characteristics, and results in production of a usable transistor.

From results of the previous sections it is well established that etched surfaces treated with reagents in which germanium dioxide is soluble provide point contact diode characteristics unsuited to electrical pulse forming.

It is often assumed, on the basis of the results of Valdes,[5] that forming effects result from the diffusion of impurities from the point into the semiconductor during the forming pulse. Since the high temperature required for such diffusion results from the power dissipated at the metal

to semiconductor contact, more efficient forming probably results on surfaces which display very low initial saturation currents. On surfaces which produce a poor initial rectifying diode, the local energy of the forming pulse may be dissipated too far out into the bulk of the semiconductor. This situation would result in inefficient forming.

Since the low-voltage diode characteristics and the forming are probably related, one should be able to predict the "formability" of any particular surface. Fig. 16 shows that this can be done qualitatively. In the graph each point represents the average of at least five units formed on electro-etched surfaces to the forming objective, $V_c(3, -5.5) \leqq 2.0$ volts. Fig. 16(a) represents the reverse emitter current before forming plotted on a log scale versus the percentage of units taking more than five pulses to form. The reverse emitter current rather than the reverse collector current is a desirable preforming parameter to use since this pre-

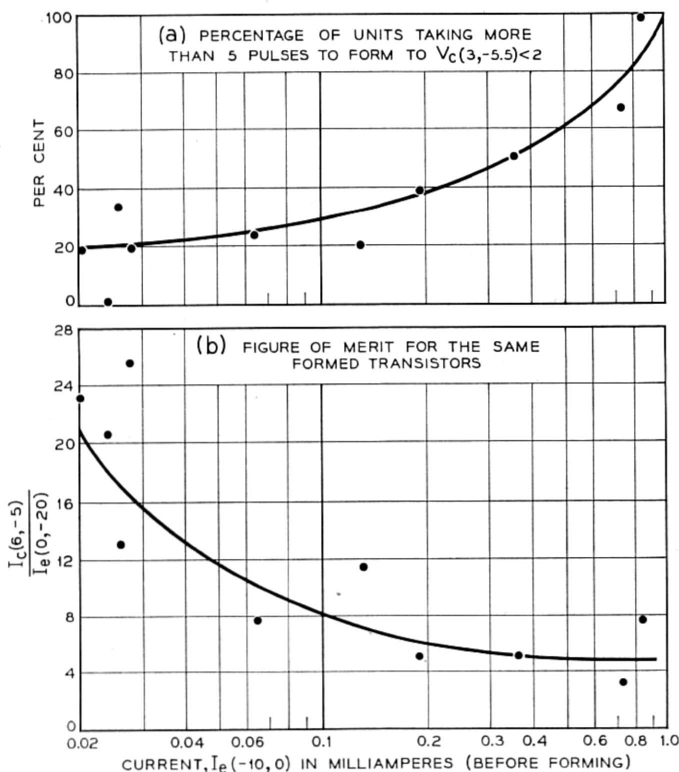

Fig. 16 — Relation of forming to pre-forming characteristics: electro-etched surfaces.

cludes any premature forming which could occur. This curve shows that a low reverse emitter current (high back impedance) is associated with easy forming and that a high reverse emitter current is associated with hard forming. Fig. 16(b) represents data on the same group of units with $I_c(6, -5)/I_c(0, -20)$ plotted versus the reverse emitter current on a log abscissa. It is significant to note that the figure of merit is consistently high for units with low reverse emitter current and low for units with high reverse emitter currents. It was possible to achieve this wide range in reverse currents on the same material by adjusting the current density in the manner summarized by Table V. In each case a high current density results in the low reverse currents.

Some other oxidizing agents may be used interchangeably with the materials just discussed. A dilute nitric acid solution produces a surface on which excellent diode properties are observed and good forming results on these surfaces. It has also been found that a treatment in potassium cyanide results in a surface which appears to be well oxidized. There are, however, some indications that certain chemical treatments tend, more than others, to passivate the germanium surface to any subsequent treatment.

Although it has been shown that variations in the surface oxide layer markedly affect the transistor made on that particular surface, variations in forming yield such as illustrated by the manipulator line in Fig. 13 are still unaccounted for. The etching procedure in the fabrication of the point contact transistor has always been one of the most carefully controlled steps. It therefore becomes necessary to examine the process for some subtle interaction between the germanium surface and the ambient to which the surface is subjected during processing.

4.2.3 *Controlled Ambient Experiments*

The experiment summarized by Fig. 17 represents a "dry box" experiment designed to investigate the effect of ambient on the forming yield. Ten germanium wafers were mounted on hermetic seal headers, they were electro-etched, and then five treated for one minute in HF. The wafers were rinsed in deionized water, dried for three minutes in a stream of nitrogen, and placed in a nitrogen dry box where the relative humidity was maintained at less than 1 per cent. One micromanipulator transistor was formed on each wafer immediately and then at subsequent intervals of one day, always in widely different locations on the wafer. These manipulations were carried out inside the dry box using rubber gloves so that at no time was the RH greater than 1 per cent. After two days the box was opened to room air and the experiment continued.

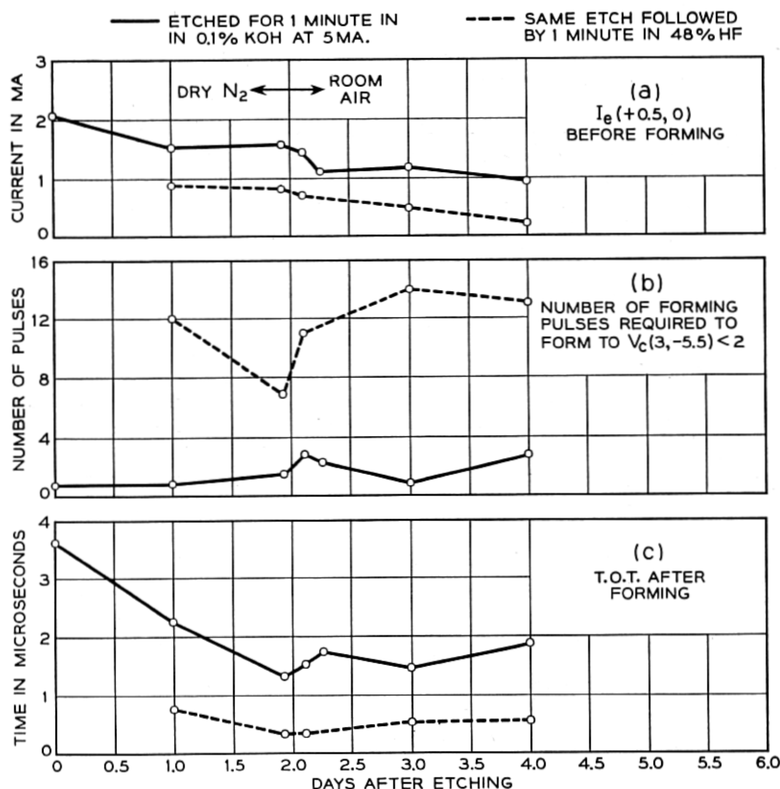

Fig. 17 — Effect of storage ambient on transistor characteristics — electro-etched surfaces.

Each point on Fig. 17 represents the average of five units on five different wafers.

The difference in the electrical properties of the two surfaces in air already noted in previous sections is observed. In addition an increase in surface recombination is indicated on the HF treated surface by a decrease in the turn-off-time measurement (TOT).* Finally, any influence of ambient on the electrical properties of the two surfaces used is apparently small.

4.2.4 *A Statistical Survey Experiment on Transistor Forming*

The experiment described here was designed to check some of the effects noted in earlier sections as well as to investigate possible interactions between the germanium surface and various ambients experienced during the processing of point contact units. The experimental design

* TOT is a nonparametric measurement indicative of the switching speed when used in a specific circuit.

TABLE IX — EXPERIMENTAL DESIGN OF RANDOMIZED BLOCK EXPERIMENT

Ambient Shelf Conditions	Surface Treatments					
	A Normal Superoxol Etch	B Electro Etch 5 ma. for 1 min. in 0.1% KOH	C 1 min. H_2O_2 after Normal Etch	D 1 min. H_2O_2 after Normal Etch and Shelf in Ambient	E 1 min. HF after Normal Etch	F 1 min. HF after Normal Shelf in Ambient
Formed immediately after treatment	x	x	x	x	x	x
Formed after shelf in room ambient	x	x	x	x	x	x
Formed after shelf over drierite	x	x	x	x	x	x
Formed after shelf in dry N_2	x	x	x	x	x	x
Formed after shelf at 76.5% RH	x	x	x	x	x	x

Note: Shelf represents storage for 24 hours.

used is a 5 × 6 randomized block experiment with multiple subgroups.[28] Table IX shows the general plan of the experiment. The six columns represent different etch treatments, and the five rows represent some possible variations in storage conditions. Each subgroup represents five transistors, and the experiment represents a total of 150 transistors made on germanium from the same zone-leveled slice, given 30 different treatments. Although nine measurements were made for each transistor, the figure of merit appeared to be most significantly dependent on the treatments.

As expected from the results already quoted, the major variability was found in units formed on surfaces freshly treated with HF, with considerable improvement in formability during storage. However, the looked for influence of storage ambients does not appear when the column F has been removed from consideration. One concludes that the variation between treatments is small, and the effect of ambient is even less than the effect of the treatments. Thus when surface treatment does not vary to extremes, the effect of storage ambient is relatively minor. Thus variations found in such experiments as exemplified on the manipulator line in Fig. 13 must be attributed to a still unknown factor.

4.2.5 *Effect of Contamination Before Etching*

Since etching removes the damaged surface and is usually done with highly corrosive materials, it seems unlikely that any contamination

before etching could affect the efficiency of etch. There have, however, been some indications that this does occur. Certain chemical treatments appear to passivate the surface to any subsequent treatment, for example, the results in Sections 4.2.3 and 4.2.4. The electro-etched surface followed by an HF treatment does not change rapidly with time in room air, while the superoxol-etched surface followed by an HF treatment changes quite rapidly. Surfaces which have been etched in CP_4 and subsequently treated in HF appear to be as stable as electro-etched surfaces. Subsequent treatments in superoxol do not appear to result in significant changes in the surface characteristics. Experiments on unetched germanium wafers indicate that none of the components of CP_4 alone will prevent normal etching, but if an unetched wafer is treated with a combination of 50 per cent nitric acid plus 48 per cent HF for a few moments, the surface will be stabilized as to retard the formation of the normal pyramidal etch pattern when the surface is etched in superoxol etch. Taken together these observations may imply that certain types of oxide surfaces are more stable than others and perhaps may even be passivated to subsequent environmental conditions.

With this background of information it becomes more believable that chemical treatments before etching could affect the surface of the germanium resulting from the subsequent etching. It is not unreasonable to believe that any variation in surface potential resulting from pre-etch treatment might influence the reaction between the etchant and the germanium. An experiment was performed using gold-bonded bases to isolate the contribution of the solder flux normally used in the base-wafer attachment. Twenty wafers from the same slice were divided into four subgroups of five. The groups were treated in such a way that any effects of HF or solder flux soaking before superoxol etching could be detected.

The results of this experiment do indicate that presence of flux before etching significantly affects the collector currents and turn-off time of transistors made on such surfaces. Although there was no apparent difference in forming yield between sub-groups, it is felt that this variation would show up as a difference in forming yield in a process where the forming efficiency is decreased somewhat by the impregnant.

4.3 *Conclusions*

Treatment of an etched surface with germanium dioxide solvents such as HF or KOH degrades the surface to such an extent that transistor forming efficiency is decreased. A similar effect is produced by corrosive flux and heat. Thus, pre-forming measurements may be used to predict

the formability of a particular germanium surface. It is shown that poor diode characteristics are usually associated with poor forming yields. One convenient way of controlling the diode characteristics to ensure successful forming is to etch electrolytically. High current density results in the most desirable surface characteristics. Electro-etched germanium which has been subsequently treated in hydrofluoric acid shows little tendency to oxidize either in room air or dry nitrogen ambient, while superoxol-etched germanium, given the same HF treatment, changes quite rapidly in room air presumably due to oxidation of surface. Sullivan[25] has also observed differences in the stability of electro-etched and chemically-treated surfaces.

Different surfaces can be prepared chemically which show more than the amount of variation normally found in pilot and manufacturing process lines. However, extreme variations in storage ambients have relatively little significant effects on any of these surfaces. It is therefore concluded that although certain chemical treatments may affect forming, the variations in process yields are not attributable to interaction between the germanium surface and storage ambients.

The results of Sections 4.2.2 and 4.2.3 suggest the possibility of passivation of the germanium surface. An electro-etched surface followed by an HF treatment exhibits a higher degree of stability to ambient than does a superoxol-etched surface treated in the same way. Treatment of a lapped germanium surface with two components of CP_4 ($HF + HNO_3$) will inhibit subsequent etching in superoxol.

The possibility that contamination *before* etching may affect the characteristics of the germanium surface after etching is considered. Experiments show that contamination of the germanium with corrosive zinc chloride-ammonium chloride flux before etching significantly affects the rectification properties of the germanium surface obtained after etching. The surface recombination velocity (in so far as it is determinative of the turn-off time of the transistor) is also significantly affected. However, on the basis of the results quoted here, it is not possible to conclude that such contamination can account for an appreciable amount of the unassignable variability in forming yields experienced in pilot and manufacturing process lines involving soldered base-wafer connections.

5. GENERAL CONCLUDING REMARKS

The experiments which have been described have implications which are important in both design and processing of point-contact transistors. These are summarized below:

5.1 *Point-Contact Transistors with High Current Gain*

In most switching applications the combination of high current gain and low reverse current is desirable. The measurements of current gain, taken together with the potential probe measurements in Section 2.2.1, indicate that, for the structures used here, the reverse collector current at operating voltage must be large enough to set up a substantial drift field before efficient collection of holes can occur. If this condition is not met, either the unit has low gain at all values of emitter current (unformed), or develops a bistability of the kind described in Section 2.3 (partially formed). For a given structure, the drift field can be increased by increasing resistivity of the germanium at the expense of increased base resistance. Here thermal stability of the contact also provides a limit. A more likely expedient, in the case of germanium, is to decrease the area of the formed collector junction by using sharper points and modified forming technique. The limits here are produced by reliability requirements for mechanical stability of the point structure.

5.2 *Current Multiplication in Unformed Transistors*

Many experiments have reported on junction transistors with high current gains which are attributable to the p-n hook mechanism. The high values of current gain observed with conventionally formed point contact transistors have been attributed to various mechanisms, among which is the hypothesis of a p-n hook structure,[6] primarily in the bulk of the germanium, introduced by the pulsing of the donor-doped point. In particular, at small emitter currents small signal α-values in conventionally formed collectors may reach values as high as ten, and values of α as large as 100 are encountered in formed collectors exhibiting anomalous output characteristics. However, the average α over a 6-ma emitter current range is usually near the value of 3.1 which would be expected from the mobility ratio of holes and electrons with the Type-A transistor geometry. The increase in reverse current of a formed collector by addition of donor to the point wire may result from the production of a hook structure. However, information is needed concerning the importance of the hook structure in accounting for the high values of α encountered at low emitter currents, or in connection with collector characteristic anomalies in conventionally formed point-contact transistors.

The unformed transistors discussed in this article differ from electrically formed units in that the collector barrier is the one at the metal-semiconductor surface. It has been found that certain chemical treatments can produce a collector barrier which allows an increased reverse

current flow and a substantial drift field near the emitter. Some of these units show an α value at all emitter currents quite comparable in magnitude to that of conventionally formed collectors, and surface treatment alone can also introduce in these unformed collector characteristics anomalies similar to those found in some formed units. It is difficult to visualize a p-n hook structure arising at the germanium surface as a result of the chemical treatments discussed. If such a possibility is precluded, the p-n hook mechanism does not seem necessary to the attaining of high α values at low emitter currents, or an α emitter current dependence of the kind normally observed in anomaly-free units. To account for values of α obtained with unformed collectors at low emitter currents, other mechanisms, such as the suggestion of Shockley, involving hole trapping in the germanium under the collector point[6, 7] or the suggestion of Van Roosbroeck,[29] involving conductivity modulation, might in this case be more suitable.

Further, unformed transistors made by appropriate chemical treatments can duplicate qualitatively the electrical characteristics of conventionally formed units, including alpha-emitter current dependence and output characteristic anomalies of types (1), (2) and (3). These phenomena can thus occur under circumstances where a well-defined hook structure is improbable.

5.3 *Surface Properties and Transistor Forming*

It has been found that a major factor in determining the forming yield of point-contact transistors is the chemical history of the surface. Thus in processing of point-contact transistors, major attention should be paid to ensuring chemical control of the base wafer surface if the forming yield is to be kept high. On the other hand, considerable variation may apparently be tolerated in storage ambients. Of course it has not been shown that such variations in storage conditions do not have an effect on subsequent reliability of the product. Processes which permit exposure of surfaces to solder fumes either before or after etching are to be regarded with suspicion. Monitoring of the reverse emitter diode characteristics should prove useful as a means of securing proper control of the pre-forming surface.

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