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LB-903

A GERMANIUM N-P-N JUNCTION TRANSISTOR BY THE ALLOY PROCESS

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Approved

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Introduction

This bulletin describes a laboratory method for the fabrication of a germanium n-p-n alloy junction transistor which is the counterpart to the germanium p-n-p junction transistor previously described in *LB-868, Germanium p-n-p Junction Transistors*. The importance of this new device arises from a fundamental difference between the two types. In the p-n-p transistor the active charge carriers are positive "holes"; in the n-p-n transistor the active charge carriers are negative electrons. Because these devices operate from power sources of opposite polarity, the two types may be advantageously combined in special circuits to eliminate components and fulfill unusual requirements. Because the electron mobility is more than twice that of holes, one of the factors affecting high-frequency response is more favorable for the n-p-n transistor than for its p-n-p counterpart.

This n-p-n junction transistor is made by fusing a binary lead-antimony alloy into each of the two opposite faces of a 0.003 inch thick wafer of 3 to 5 ohm-centimeter p-type single-crystal germanium. Since this alloy is ductile, the electrodes may be made relatively large if desired, as there is less danger of introducing differential expansion strains. The techniques and processes of assembly are similar to those employed in making the previously described p-n-p junction transistor (*LB-868*). However, an important difference arises from the more uniform penetration afforded by the binary alloy. This leads to more planar junctions and permits better control of junction spacing.

The distribution curves on a typical lot of 100 units show that the results are generally superior to those reported in *LB-868* for the p-n-p transistor; best power gain was 45 db, "alpha" 0.997 and 1-kc noise factor, 3 db. In addition, high "alpha" is maintained as the collector current is increased.

General Discussion

The n-p-n transistor is distinguished from the p-n-p type by the opposite sign of the active charge carriers which are negative electrons instead of positive holes. This difference manifests itself in the reversal of the operating potentials. This reversal of potentials can be utilized in special circuits which combine both the n-p-n and p-n-p transistors to save components and fulfill special tasks. Because the operating polarities of the n-p-n transistor are the same as those of electron tubes, the n-p-n transistor is well suited to applications where tubes and transistors are incorporated in the same circuit.

The mobility of electrons differs from that of holes in semiconductors; in germanium mobility is a factor 2.1 higher for electrons than for holes. Although this does not affect the fundamental mechanism of the transistor, it does advantageously influence ultimate high-frequency performance because the transit time between the emitter and collector junction is inversely proportional to the mobility. One of the fundamental high-frequency limitations in a transistor is the transit time dispersion which in turn is proportional to the transit time, so that the "alpha" cut-off frequency of the n-p-n transistor is theoretically more than twice as great as that of a geometrically similar p-n-p type. This fundamental frequency limitation is given by the following equation[1]:

$$f = \frac{D}{\pi W^2} = 0.008 \frac{\mu}{W^2} \qquad (1)$$

where f is the frequency at which "alpha" squared has dropped to half of its maximum low frequency value. D is the diffusion constant for the carriers, μ is their mobility and W is the base section thickness or junction separation. Since Eq. (1) shows that the frequency is proportional to the mobility, the desirability of the higher mobility of electrons as current carriers is obvious. It is also evident that the junction separation must be kept as low as possible for high-frequency transistors.

The n-p-n transistor consists of a thin section of p-type germanium between two n-type sections. To produce this structure by the alloying technique, p-type single-crystal germanium is required. The junctions are obtained by alloying the germanium surface with a molten n-type impurity from both sides of a thin germanium wafer. Although diffusion plays a part at the alloy-germanium interface, the overall process is called "alloying" since it is so different from the pure diffusion which takes place in the solid state. N-type impurities are, in most cases, solids at room temperature and have to be liquified at elevated temperatures, which also accelerate the alloying process.

The physical principles governing the design of alloy junction transistors and the practical techniques of construction have been described previously in connection with the p-n-p junction transistor[2]. The same considerations are applicable to the n-p-n alloy junction transistor so that the following discussion is restricted to problems peculiar to the n-p-n type.

Materials and Alloying Process

Natural sources of germanium yield chiefly n-type germanium after reduction of the oxide. Therefore it is necessary to purify the n-type material to a purity well above the desired p-type impurity concentration[3]. This highly purified germanium is then "doped" in the melt with a suitable p-type impurity whose concentration is dictated by the desired germanium resistivity[4]. Although germanium resistivities between 0.7 and 17 ohm-centimeter have yielded satisfactory n-p-n transistors, the most reproducible results in the present work have been obtained in the resistivity range between 2 and 7 ohm-centimeters. Gallium and indium have been used successfully for the doping, but indium has the advantage of being solid at room temperature and was used in most of the germanium crystals employed.

Transistor theory indicates that it is desirable to use p-type germanium with high lifetime of the minority charge carriers (electrons), preferably in excess of 10 microseconds. The germanium must be a single crystal because the grain boundaries in polycrystalline material constitute recombination planes where minority carriers are lost, thus reducing the lifetime.

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[1] W. Shockley, M. Sparks, G. K. Teal, "P-N Junction Transistors", *Phys. Rev.*, Vol. 83, No. 1, p. 151, July 1951.

[2] *LB-868, Germanium p-n-p Junction Transistors.*

[3] *LB-890, Purification of Germanium by Gradient Freezing.*

[4] *LB-899, Theoretical Resistivity and Hall Coefficient of Impure Germanium Near Room Temperature.*

The n-type impurity element used to form the junction by the alloying process can, in principle, be any of the following: phosphorus, arsenic, antimony and bismuth. During the work on the n-p-n alloy junction transistor it was found that sulfur, selenium and tellurium are also n-type impurities. Extensive tests led to the selection of antimony as most suitable for the alloying impurity. Phosphorus and arsenic are less desirable due to their high vapor pressure; bismuth yields unsatisfactory junctions; and sulfur, selenium and tellurium have high electrical resistivities. Although successful transistors have been made using pure antimony, and small area junctions with antimony give excellent results, considerable difficulty is encountered as the area is increased. Due to the difference in thermal-expansion coefficient between antimony and germanium, severe strains are introduced near the antimony-germanium interface. These differential expansion strains can cause mechanical and electrical instabilities which manifest themselves in one of the three following ways. In the most serious case, the strain forces may be so large that actual breakage occurs and the antimony is separated from the germanium by sudden cleavage of the germanium near the interface. If separation does not take place, there may be internal breaks of microscopic dimensions which cause electrical instabilities due to contact pressure fluctuations and, possibly, fluctuating lattice distortions. In this case, the transistor exhibits random gain fluctuations which are clearly noticeable during a gain measurement. Even if the gain appears to be stable, the strains influence the noise factor considerably and extremely high noise is observed when strains are present. This interpretation is supported by the noise-reducing effect of annealing and the increase in noise due to thermal quenching, both of which were observed during this work.

The elimination or reduction of the differential expansion strains is possible in three ways, namely, by devising an impurity-containing material whose thermal-expansion coefficient approximates that of germanium, or whose ductility is large, or whose melting point is close to room temperature. Although it does not seem possible to fulfill the above requirements with a single impurity element, there are alloys of two or more phases containing an n-type impurity which satisfy one or more of the strain relief conditions. A simple solution is a binary alloy of antimony and a ductile n-type or neutral metal which does not interfere with the formation of the junction. Of the many alloys which were investigated, the lead-antimony system was found to be the most successful.

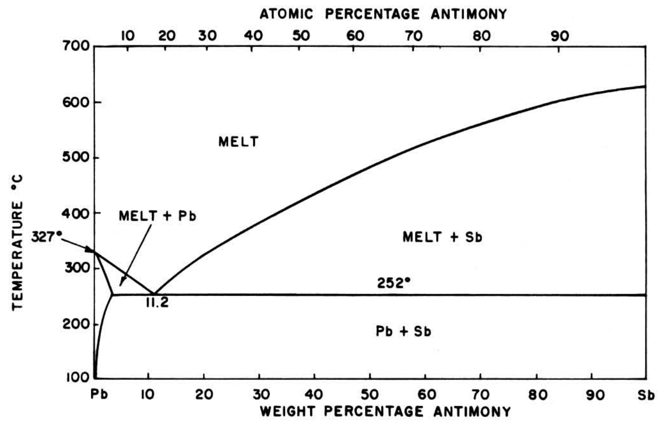

Fig. 1 - Phase diagram of the lead-antimony system.

In Fig. 1, representing the phase diagram of lead and antimony, a eutectic with a melting point of 252 degrees Centigrade is present at 11.2 per cent antimony. This eutectic is relatively ductile, compared with antimony, and in addition has a considerably lower melting point than pure antimony. It was found that alloys on the antimony-rich side of the eutectic still introduce strains due to the separation of antimony crystallites during the solidification process, so that it is desirable to choose a lead-rich composition. A 10 per cent antimony-lead alloy was found to be excellent for forming alloy junctions on p-type germanium. Lower antimony contents yield junctions with increasingly higher forward resistance, which is undesirable for the emitter junction of a transistor. Although similar mechanical properties are exhibited by tin-antimony alloys, the metallurgical behavior is sufficiently different to yield unsatisfactory junctions.

The formation of an alloy junction is governed by the following most important factors: wetting of the germanium by the impurity substance, and solubility of the germanium in the impurity substance. The wetting is dependent on the surface tension of the molten impurity and determines the shape of the junction plane, whereas the solubility determines the penetration depth and also has an effect on the junction shape.

Fig. 2 gives hypothetical characteristic stages during the formation of an alloy junction. As shown in (a) the impurity metal disk is put on the germanium surface and (b) contracts to form a sphere upon melting after which (c) the contact area is enlarged by the wetting process as germanium is being dissolved, and (d) the final configuration is reached after solidification by cooling to room temperature.

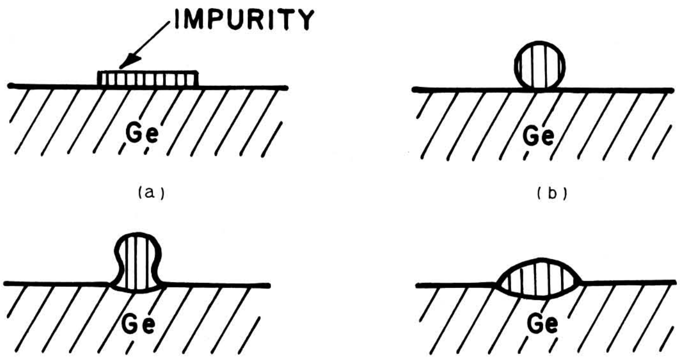

Fig. 2 - Formation of an alloy junction in four subsequent steps.

As it is desirable to obtain a planar junction, the wetting process must take place as rapidly as possible and preferably at a temperature at which the solubility of germanium in the impurity element is still small. This aids a uniform penetration of the alloy front over the whole junction area and therefore yields a planar junction. Because the wetting is accelerated by a low surface tension, and the latter is an inversc function of temperature, it is recommended that the processing temperature be increased as rapidly as possible in the beginning of the firing. For the same reason, it is desirable to process at as high as possible a temperature. In an alloy junction transistor it is in general advantageous to keep the alloying depth low, which requires a low solubility of the germanium.

The limit of the alloying depth is determined by the liquidus curve in the germanium-impurity phase diagram which is shown for lead-germanium in Fig. 3. Although the conditions are somewhat different for the tertiary lead-antimony-germanium system, which occurs in the n-p-n alloy transistor, Fig. 3 is an acceptable

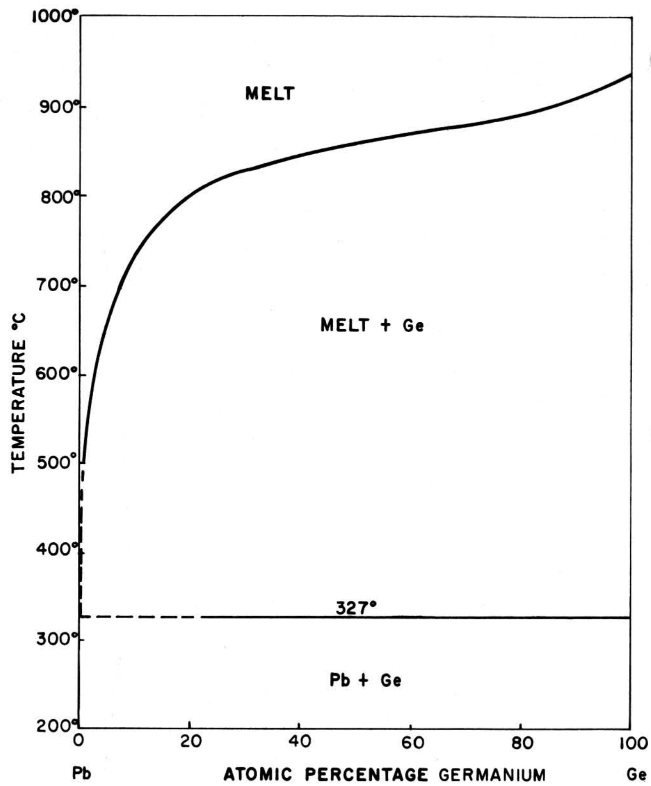

Fig. 3 - Phase diagram of the lead-germanium system.

approximation due to the low antimony content in the impurity alloy. The penetration depth limit is approximately represented by the distance between the temperature axis and the liquidus curve at the processing temperature. Due to the steepness of the liquidus line up to about 700 degrees Centigrade, the depth varies little compared with the region above 800 degrees Centigrade. Therefore the processing temperature is relatively uncritical below 700 degrees Centigrade as was verified experimentally.

In conclusion, it is evident that a steep liquidus curve of the impurity-germanium system on the impurity side is desirable to render the alloying process less critical as to temperature. The upper temperature limit is determined by the break in the liquidus curve, and processing ought to be as close as possible to this limit due to the high temperature requirement for rapid wetting.

Techniques and Processing

The practical laboratory techniques of construction of alloy junction transistors hav been described in *LB-868*, and reference is made to this bulletin for details. The steps are briefly summarized below and, where deviations peculiar to the n-p-n transistor occur, a detailed description is given.

Single-crystal p-type germanium, with a resistivity between 2 and 7 ohm-cm, is cut into wafers of 0.012-inch thickness and 1/16-inch x 1/8-inch size. These wafers are then surface-ground to a thickness of 0.008 inch and etched to a thickness of 0.003-inch. A suitable etching solution is:

70 per cent Nitric Acid	5 parts
52 per cent Hydrofluoric Acid	5 parts
Distilled Water	1 part

The lead-antimony alloy is cleaned by a mild etching before being applied, a suitable solution for which is:

99½ per cent Glacial Acetic Acid	3 parts
30 per cent Hydrogen Peroxide	1 part

These wafers are then placed into the special graphite boat described in *LB-868*, and a 0.015-inch thick disk of the 10 per cent antimony-lead alloy with a diameter of 0.045 inch is placed in the center and positioned by a graphite washer. This assembly is fired at 650 degrees Centigrade for 5 minutes in a dry and deoxidized hydrogen atmosphere. After this the wafer is turned over so that the alloyed impurity dot fits into the positioning hole at the bottom of the graphite boat. Another lead-antimony disk of the same thickness, but with a diameter of 0.015 inch, is positioned by a graphite washer on the upper side of the wafer. In addition, a small nickel tab, which has been tinned at one end, is placed with the solder-coated end on the germanium wafer, just as described in *LB-868* for the p-n-p transistor. The assembly is then fired at 650 degrees Centigrade for 10 minutes in a similar hydrogen atmosphere. The cooling to room temperature must be carried out slowly and should not exceed a rate of 40 degrees Centigrade per minute.

The junction surfaces are then cleaned and conditioned by etching. This final etching is carried out in two steps with two different etching solutions. The composition of the first etching solution is:

70 per cent Nitric Acid	80 parts
52 per cent Hydrofluoric Acid	50 parts
99½ per cent Glacial Acetic Acid	50 parts
Bromine	1 part

The second etching solution has the following composition:

70 per cent Nitric Acid	1 part
52 per cent Hydrofluoric Acid	1 part
Distilled Water	1 part

The fired transistor unit is dipped into the first etching solution for 5 seconds and subsequently into the second solution for another 5 seconds without washing in between. During the etching process it is important to prevent the nickel tab and the solder from coming into contact with either of the etching solutions, so that there is no contamination of the junction surfaces by electrolytic redeposition of dissolved nickel or solder. On the other hand, complete immersion of the junctions is imperative to allow uniform action over the whole exposed junction area. The unit is then washed in hot water of at least 80 degrees Centigrade for not less than 5 minutes during which the black deposit on the antimony-lead alloy is dissolved and the appearance becomes dull gray.

The transistor unit is mounted by welding the nickel tab to the center lead of a three-lead glass stem and making Cerrobend solder connections of the junctions to the outer two leads. The entire unit is dipped in Amphenol coil dope and after drying is dipped in black enamel. Finally, the entire unit is potted in ethoxylene casting resin containing titanium dioxide. The details of this mounting and potting procedure are described in, and the units have the same physical appearance as those of *LB-868*.

Electrical Characteristics

Units of the n-p-n alloy type, made as described herein, have been given the experimental designation TA-154. Electrical characteristics have been taken on over a hundred early units and do not necessarily represent the ultimately attainable characteristics. The TA-154 is primarily intended for small-signal applications at low frequencies. The discussion and data are presented with emphasis on the base-input (common emitter) connection which has found extensive application in apparatus. In this circuit the similarity between electron tube and junction transistor facilitates the understanding and design of the allied circuitry. For a description of the testing techniques and apparatus used in taking the data, reference is made to the respective Industry Service Laboratory Bulletins, *LB-871, Dynamic Test Set for Transistors; LB-876, Noise Factor Measurements of Transistors;* and *LB-882, A Transistor Curve Tracer.*

The characteristics of a transistor can be presented in several different ways, each of which has its merits. A common representation consists of the resistance values in the equivalent T-circuit as shown in Fig. 4, which describes the transistor at low frequencies, and with small signals.

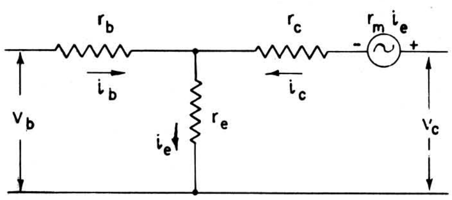

Fig. 4 - Equivalent T circuit of an n-p-n junction transistor in the base input (emitter common) circuit.

At higher frequencies, capacitances have to be introduced and the evaluation becomes more complicated. The derivation of the various transistor characteristics from the resistance values is described in the literature[5]. The ranges of resistances which can be achieved for n-p-n alloy junction transistors, when made by variations of the procedure described in this bulletin, and operated at 2-ma emitter current, are of the order of

$$r_b = 100 \text{ ohms to } 2500 \text{ ohms}$$
$$r_e = 2 \text{ ohms to } 20 \text{ ohms}$$
$$r_c = 100{,}000 \text{ ohms to } 10 \text{ megohms}$$
$$r_m = 100{,}000 \text{ ohms to } 10 \text{ megohms}$$

The r_b is strongly dependent on the germanium resistivity and can be decreased by using low resistivity germanium. The r_c is a measure of the quality of the collector junction and is greatly affected by the etching process. r_e is to some extent determined by the forward characteristics of the emitter junction. Finally, r_m is to a first approximation proportional to the current gain "alpha" and it is always lower than r_c in this type of junction transistor.

The properties of a transistor may also be described by static characteristics similar to the well-known electron tube presentation. Due to the finite input impedance of the transistor it is not sufficient to give only the output characteristics with the input potential as parameter. An adequate picture of the transistor behavior can be obtained from a set of four curve families as are shown for a typical experimental TA-154 in Figs. 5 to 8.

The static characteristics suffice, in principle, for the analysis of amplifier operation by applying suitable load lines to the curve families. In practice, however, small-signal evaluation requires more accurate data than can be derived from static curves taken with a curve tracer.

The most explicit way of representing the transistor characteristics consists in the actual measurements of the important characteristics such as power gain, current gain, noise factor, etc. under various bias and impedance conditions and at different frequencies. A full description of a transistor would require a large number of curves, but by suitably choosing the test conditions it is possible to cover the most important application cases. In Figs. 9 to 14, a set of curves describing the important parameters of typical TA-154 transistors are reproduced. Except for the frequency dependence data the same TA-154 was used for these data.

The current gain in Fig. 9 is observed to be essentially constant from 2 to 10 milliamperes, which range corresponds to a current density of several amperes per cm^2. Similarly, the variation of the power gain with collector potential is negligible between 2 and 10 volts as shown in Fig. 10. The source impedance of 500 ohms and the load impedance of 10,000 ohms are chosen to be in the vicinity of the average matching impedances for maximum power gain at an emitter current I_e of 2 milliamperes and a collector potential V_c of 6 volts. The operating currents and potentials are of arbitrary choice

[5] R. L. Wallace and W. J. Pietenpol, "Some Circuit Properties and Applications of n-p-n Transistors", *Proc. I.R.E.*, Vol. 39, p. 753, July 1951.

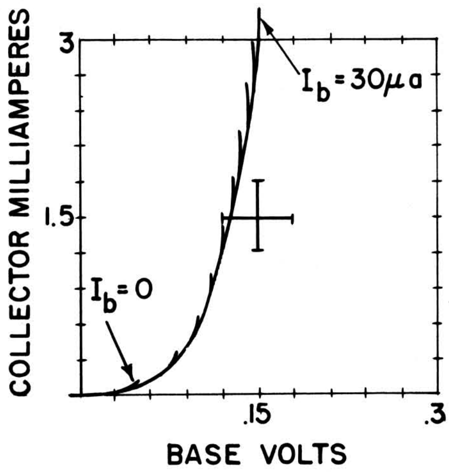

Fig. 5 – Transfer characteristics of a typical TA-154 junction transistor (base current I_b in ten equal steps from 0 to 30 microamperes).

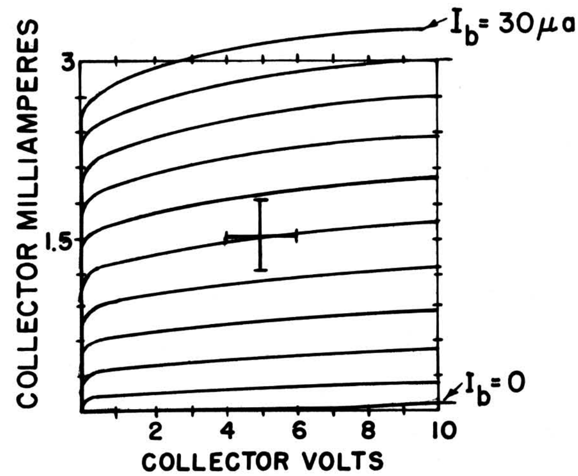

Fig. 7 – Output characteristics of a typical TA-154 junction transistor (base current I_b in equal steps from 0 to 30 microamperes).

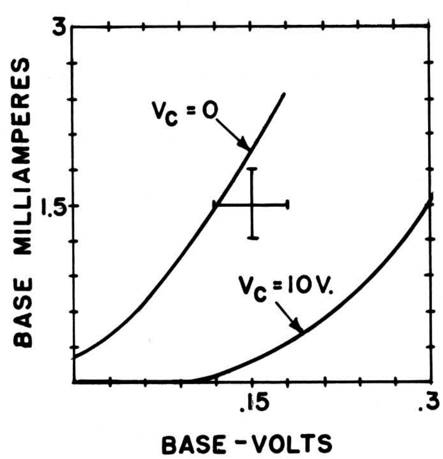

Fig. 6 – Input characteristics of a typical TA-154 junction transistor (collector potential V_c equals 0 and 10 volts).

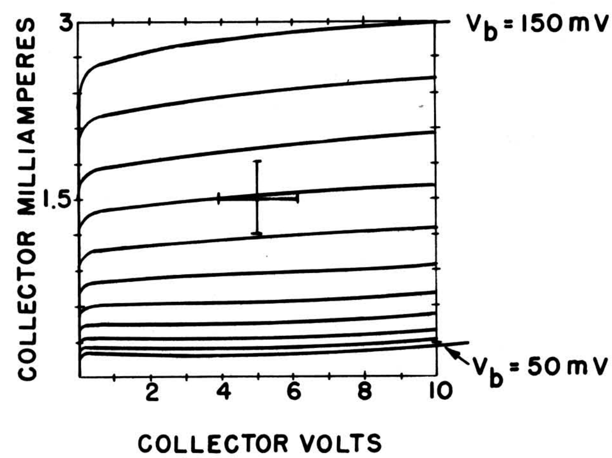

Fig. 8 – Output characteristics of a typical TA-154 junction transistor (base potentials in 10 equal steps from 50 to 150 millivolts).

but lie within the most probable application range.

The noise factor results in Figs. 11 and 12 show that, in general, an increase in potential or current raises the noise, and a minimum noise factor is reached at about 1 volt collector potential and 1 milliampere emitter current.

In the audio range, the noise factor is inversely proportional to the frequency, so that the 1000-cycle value is readily interpreted. The 560-ohm source impedance corresponds approximately to the matching impedance for maximum power gain as pointed out above.

Although the TA-154 was intended only for audio-frequency applications, the performance at higher frequencies is of interest. One measure of the behavior of a transistor at higher frequencies is the current amplification factor, as pointed out in the general description. In Fig. 13 the limits represent the results on early units of the TA-154 and it can be seen that the spread is considerable at the high frequency end.

A direct gain measurement under conditions with a resistive input and conjugate-matched output gives a more useful picture of the high-frequency behavior as shown in Fig. 14. Presumably if a conjugate match adjustment had been available for the input, the gains would have been very slightly higher. The average, and the high, power-gain vs frequency curves up to about 1 Mc show that useful gains are attained at intermediate frequency (455 kc), and selected units give significant gain in the broadcast band (500 kc to 1.5 Mc).

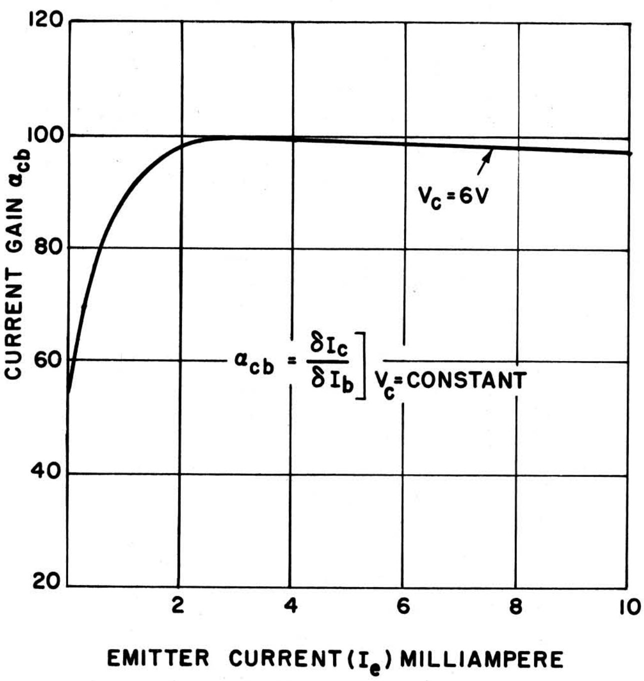

Fig. 9 - Variation of the collector-base current gain a_{cb} with emitter current for a typical TA-154 transistor.

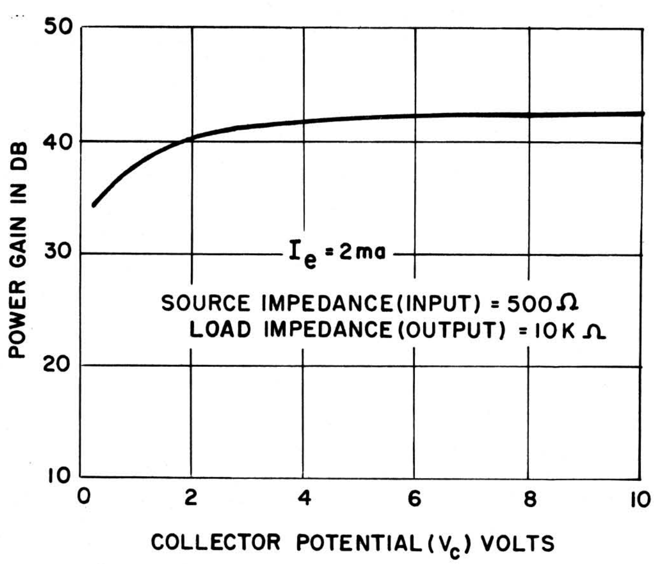

Fig. 10 - Variation of power gain with collector potential for a typical TA-154 junction transistor.

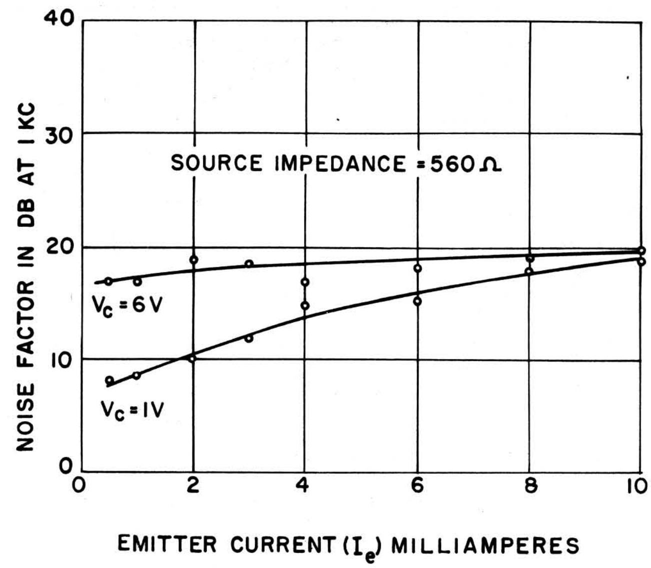

Fig. 11 - Variation of noise factor emitter current for a typical TA-154 junction transistor.

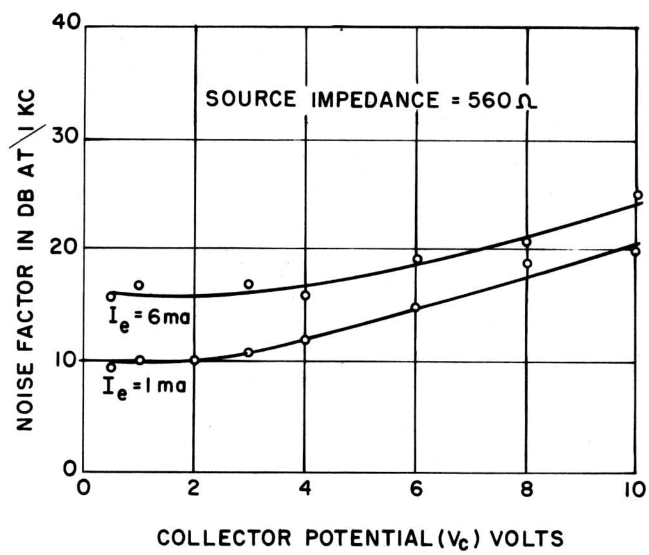

Fig. 12 - Variation of noise factor with collector potential for a typical TA-154 junction transistor.

A statistical evaluation of an early lot of 100 TA-154 transistors is presented in Figs. 15 to 17. These units were made under similar conditions and constitute all the units in this test, with the exception of mechanically damaged transistors and 21 units which were eliminated due to collector leakage currents in excess of 100 microamperes at 6 volts collector potential and zero emitter current.

The power gain peak in Fig. 15 is very pronounced at 42 db, and more than 50 per cent of the units are within the limits of 42 ± 2 db,

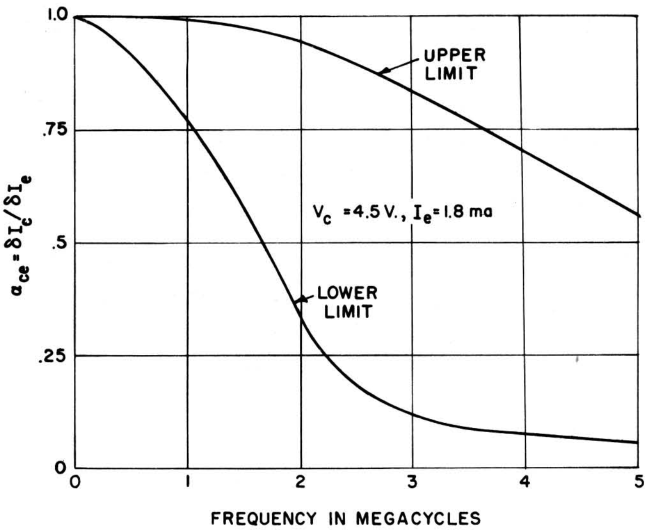

Fig. 13 – The variation with frequency of collector-to-emitter current gain, α_{ce}, for a lot of 100 TA-154 junction transistors; all units fall between the two curves shown.

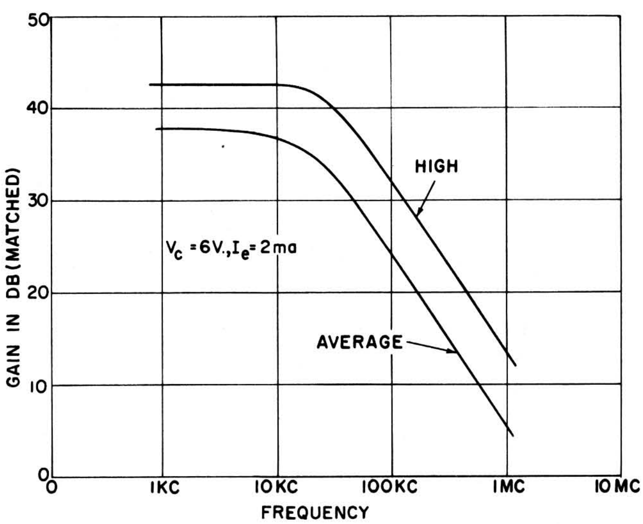

Fig. 14 – Variation of power gain with frequency for typical TA-154 junction transistors. A resistive input and conjugate-matched output were used.

although the average of all transistors lies at 38.3 db.

The current gain, α_{cb} in Fig. 16, shows a peak at about 70 and more than 50 per cent of the units are within the limits 70 ± 30. Translated into emitter input current gain α_{ce} the peak is at 0.985 and the limits for more than 50 per cent of the units are 0.985 ± 0.01. The averages are, for α_{cb} at 108 and for α_{ce} at about 0.99.

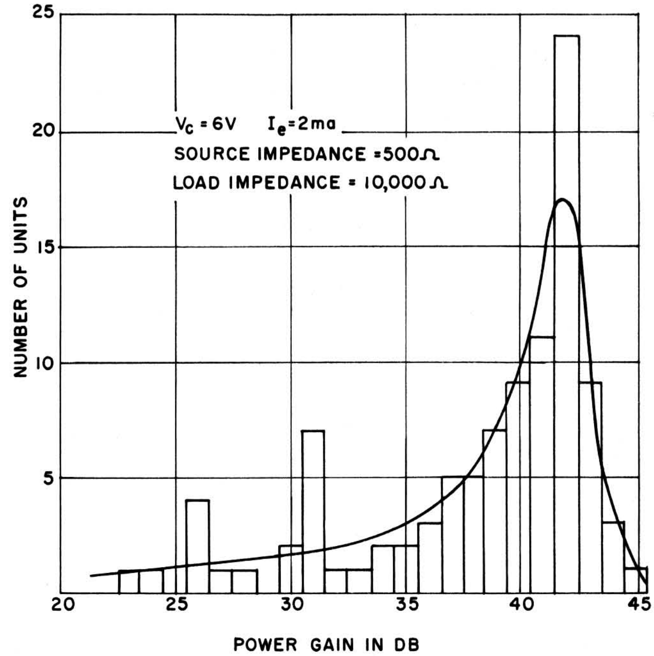

Fig. 15 – Distribution of power gain for a typical lot of 100 TA-154 transistors.

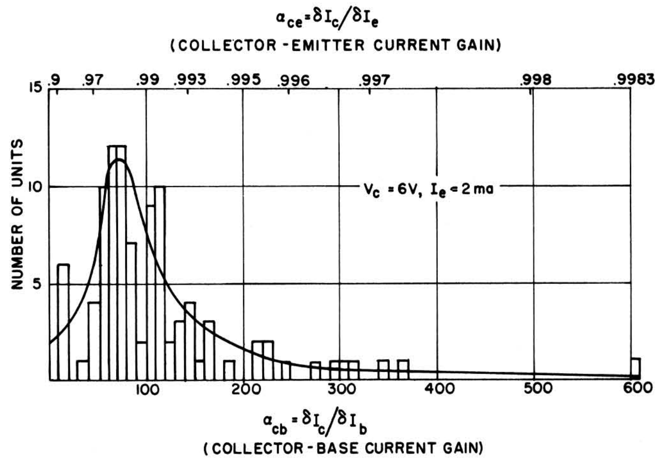

Fig. 16 – Distribution of a_{cb} (collector to base current gain) and of a_{ce} (collector to emitter current gain) for a typical lot of 100 TA-154 transistors.

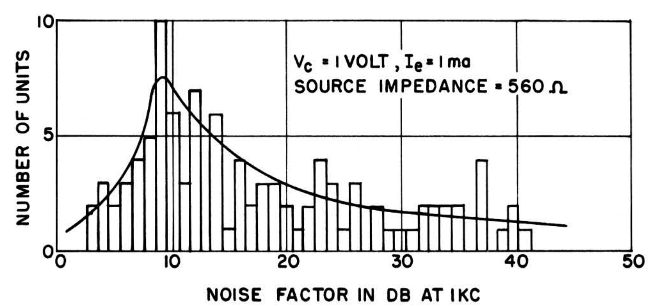

Fig. 17 – Distribution of noise factor for a typical lot of 100 TA-154 transistors.

Finally the noise factor distribution in Fig. 17 shows a peak at 9 db and more than 50 per cent of the units lie within 9 ± 5 db with the average being 17.8 db.

Conclusions

The characteristics measured on the TA-154 experimental n-p-n alloy junction transistors, as described above, are generally superior to those given in *LB-868* for an early lot of TA-153 p-n-p junction transistors. The number of units with high power gain and low noise factor is much larger, and the collector-to-base current gains are higher. Also of significance is a practically constant current gain as the collector current is increased, which was not exhibited by the data taken on the early TA-153 units, as given in *LB-868*. Finally, there are at least preliminary indications that the TA-154 yields a larger proportion of units having exceptional high-frequency response.

D. A. Jenny

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Appendix

RCA Laboratories Experimental N-P-N Junction Transistor TA-154

Preliminary and Tentative Data

N.B. Do not accidentally interchange p-n-p with n-p-n transistors in operating circuits. The reversed battery polarity may easily be highly damaging to the units.

Physical Specifications:

1. *Green* dot on side identifies the emitter.
2. Center pin is the base; the remaining pin is the collector.
3. Pin spacing fits Cinch 2H5 subminiature socket or equivalent

Mounting Position . . . . Any

CAUTION: When solder connections are made, heat-sink protection on the transistor side of the joint should be provided.

Maximum ratings, physical size limits, etc., have not been established. The collector potential should not exceed 20 volts and the power dissipation must be kept below 50 milliwatts at 25 degrees C ambient.

*Typical Operating Values at 25 degrees C.** Base input connection (emitter grounded)

V_c (collector potential) with respect to base. . . . . . +6 volts

I_e (emitter current) . . . . 2 milliamperes

Source (input) impedance . . . . 500 ohms

Load (output) impedance . . . . .10,000 ohms

Power gain (with above source and load impedances) . . . . >40 db

$\alpha_{ce} = -\partial I_c/\partial I_e$ (collector-emitter current gain). 0.99

$\alpha_{cb} = -\partial I_c/\partial I_b$ (collector-base current gain) 100

Iterative Amplifier Gain (direct coupling with no impedance match) . . . . .40 db

Noise Factor (V_c = 1 volt, I_e = 1 milliampere, 1 kilocycle .15 db

(Source impedance = 500 ohms, load impedance = 10,000 ohms)

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*The transistor should not be subjected to excessive surge currents as may occur on plugging in or removing the unit with the power on.

Reference: Wallace and Pietenpol, "Some Circuit Properties and Applications of n-p-n Transistors", *Proc. I.R.E.*, Vol. 37, p. 753, July 1951.