

## METHODS OF PRODUCING STABLE TRANSISTORS

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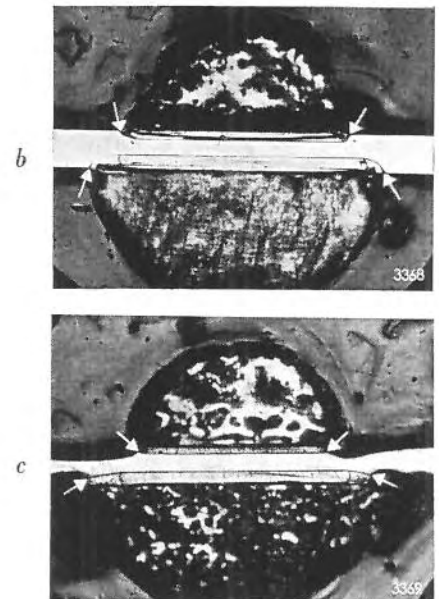
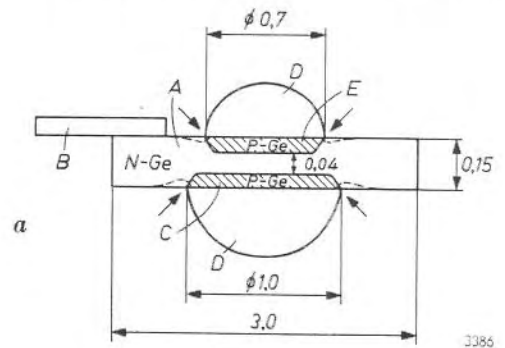
*One of the major problems in the manufacture of transistors is to make them stable, i.e. to produce transistors whose characteristics do not change in the course of time. Such changes are due to surface effects. It is therefore necessary to produce surface conditions that will minimize these changes.*

It was originally hoped that the characteristics of junction transistors, by their very nature, would change very little and that, if properly used, the transistors would have an almost unlimited life. Theoretical considerations show that the operation of these transistors is governed by the dimensions and the material properties of the constituent layers, i.e. of the emitter, base and collector<sup>1)</sup>, and there is no reason to assume that these dimensions and properties alter in normal operation. At places where the *P-N* junctions reach the surface (see *fig. 1*) there must of course be no surface layer that might give rise to an undesired conductive path between the *P* and *N* regions. In the fabrication of transistors, cleaning the surface by etching is therefore one of the routine operations.

The optimistic expectations regarding the stability of transistors have not been borne out, however. It very soon appeared that, in spite of the etching, the state of the germanium surface has a very pronounced influence on the properties of the transistor. The electrical changes observed are very often due to changes in this surface — as, for example, the adsorption of foreign molecules and atoms — and these in their turn are bound up with the state of the ambient atmosphere. The obvious way to seek improvement was therefore to hermetically encapsulate the transistors. This, however, proved to be insufficient: life tests showed that the parameters — in particular the current amplification factor — continued to change. The production of stable transistors was more difficult than was at first thought.

In many laboratories the surface of germanium, and semiconductor surface phenomena in general, have consequently been the subject of much experimental and theoretical research<sup>2)</sup>. One of the aims pursued was to find methods of achieving surface

conditions that would result in good transistors and moreover ensure a high degree of stability. This article will describe some results of investigations



*Fig. 1. a) Schematic cross-section of a P-N-P junction transistor, made by the alloying method. Dimensions in millimetres. A germanium single crystal of type N in the form of a wafer (3 × 2 × 0.15 mm). B base contact. C collector; this part of the germanium crystal is given P-type conductivity by alloying with the acceptor material D. E emitter, also of P-type germanium due to alloying with D. The arrows indicate where the P-N junctions reach the surface. After etching, the surface follows the dashed lines. b) Polished cross-section, on which the various regions are made visible by etching. The arrows again indicate the P-N junctions at the surface. The transistor is here surrounded by a layer of shellac in connection with the preparation of the sample. c) As b), but with etched surface.*

<sup>1)</sup> See F. H. Stieltjes and L. J. Tummers, Simple theory of the junction transistor, *Philips tech. Rev.* **17**, 233-246, 1955/56, and F. H. Stieltjes and L. J. Tummers, Behaviour of the transistor at high current densities, *Philips tech. Rev.* **18**, 61-68, 1956/57.

<sup>2)</sup> R. H. Kingston, Review of germanium surface phenomena, *J. appl. Phys.* **27**, 101-114, 1956.

undertaken along these lines at Philips Research Laboratories at Eindhoven. The investigations concerned *N-P-N* and *P-N-P* germanium transistors for low frequencies and low power, made by the alloying method. A schematic cross-section of this type of transistor (*P-N-P*) is shown in fig. 1, together with the relevant dimensions.

The marked influence which the surface has on the operation of a transistor is accounted for by assuming that holes and electrons recombine at the surface to an extent that depends strongly on the state of the surface. To explain this effect, let us consider a *P-N-P* transistor. Here the emitter injects holes into the base, whilst the collector acts as a sink for holes from the base. If no recombination occurs in the base — in a stationary or quasi-stationary state — all injected holes will disappear to the collector, where they contribute to the collector current. That is the ideal situation. In fact, however, holes disappear in the base by recombining with electrons, and are thus lost to the collector current. This “base loss” is one of the two reasons why the ratio of the collector current to the emitter current — called the current amplification factor  $a$  — is less than unity<sup>3)</sup>. It has been found that the base loss in transistors of the alloy type may largely be due to recombination at the surface. Changes in the velocity of recombination at the surface therefore have a considerable effect on the base loss and hence on the behaviour of the transistor.

We shall look a little closer at the reason for this effect. If we speak of a high surface recombination velocity, we mean that a hole in the neighbourhood of the surface is very likely to be lost by recombination with an electron. Whether there is in fact a high degree of recombination near the surface depends of course on whether there are holes there to be affected. To show that this will certainly be so, we may consider the case where no recombination at all takes place at the surface. Fig. 2a

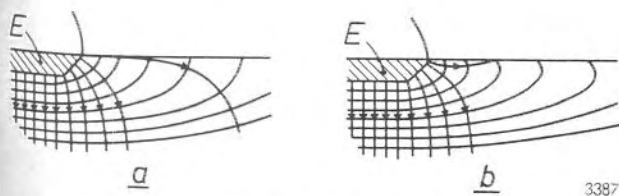


Fig. 2. Illustrating contours of constant hole concentration and the flow lines of the hole current (with arrows) in the base of a *P-N-P* junction transistor at the edge of the emitter *E*. The two sets of lines are orthogonal.

a) The pattern on the assumption that there is no recombination at the surface. The lines of constant hole concentration must then terminate at right-angles to the surface. The hole current passes along the surface; if there is any opportunity for surface recombination, holes will certainly be lost.

b) The pattern after correction for surface recombination. (Recombination inside the base is disregarded in both cases.)

<sup>3)</sup> The second reason is the emitter loss; see p. 239 *et seq.* of the first article quoted in reference 1).

roughly illustrates the flow pattern of the hole current in that case, together with the lines of constant hole concentration. The two systems of lines are orthogonal, and the lines of constant concentration must moreover terminate perpendicular to the surface. The hole current must therefore run partly along the surface, so there will indeed be holes there, which may be destroyed by recombination at the surface. The recombination calls for a correction to the pattern in fig. 2a. The corrected pattern will look something like that in fig. 2b.

To make a stable transistor it would be a great help if the surface could be treated in such a way as to make the surface recombination velocity insensitive to extraneous influences. Although work is being done in that direction, the results have so far been unsatisfactory. In this article we shall be solely concerned with the method whereby an attempt is made to reach the same objective by providing the transistor with a suitable *ambient atmosphere*. Obviously, this is possible only if the transistor is enclosed in a hermetically sealed container. We shall see presently why this air-tight enclosure is not in itself enough. There are certain substances that not only reduce the surface recombination velocity to an acceptable value but also, provided they are properly applied inside the enclosure, keep it constant over a long period of operation. Two outstanding representatives of these substances will be discussed here, namely *water* and *arsenic*, particular attention being given to the influence of water, i.e. water vapour.

A sensitive indication of the base loss, and hence of the surface recombination velocity, is the ratio of the collector current to the base current. We denote this “current amplification factor” by  $a'$ , to distinguish it from the earlier mentioned  $a$ , which is the ratio between collector and emitter currents. Between  $a$  and  $a'$  there exists the well-known relation

$$a' = \frac{a}{1-a},$$

which follows directly from the fact that the sum of the emitter, base and collector currents is zero (provided these currents are counted positive when directed towards the transistor). Since  $a$  is not much smaller than unity — at least in a serviceable transistor —  $a'$  undergoes greater changes than  $a$ . For the purpose of judging the surface effects of the various measures adopted,  $a'$  is therefore always measured.

#### The effect of water

It is known that the surface recombination velocity depends on the surface occupation by water

molecules<sup>4</sup>). When the surface is completely dry, the surface recombination velocity is high, and  $\alpha'$  is correspondingly low. As the water "occupation" increases, the surface recombination velocity decreases and  $\alpha'$  rises. The changes of  $\alpha'$  observed on transistors are therefore certainly to a considerable extent attributable to changes in the water occupation of the surface. Even in hermetically encapsulated transistors, the surface water will almost certainly be affected by temperature variations, for example. The migration of the water may be so slow that one cannot always expect to find the same value of  $\alpha'$  at the same temperature. Slow reactions involving water may also play a part.

The most obvious method of eliminating this undesired influence is to make sure that there is no water at all inside the transistor envelope. This is a method that is in fact used, but it has the drawback of resulting in a low value of  $\alpha'$ . It appears that the presence of only a minute trace of water is sufficient to make  $\alpha'$  unstable.

In the methods discussed in this article an attempt is made to create conditions inside the transistor envelope such as to give the surface of the transistor a water occupation that will ensure a high value of  $\alpha'$ , and at the same time remain constant with time and temperature.

As we have seen, the surface recombination velocity decreases if the surface water increases. At constant temperature, a state of equilibrium will be reached inside the transistor envelope between the surface water and the water-vapour pressure: the greater the vapour pressure, the more densely will the surface be occupied by water molecules, and hence the greater will be the value of  $\alpha'$ . The water-vapour pressure must not, however, be unduly high, for if the surface is too wet, disturbances are caused by superficial ionic currents, one result of which may be the appearance of loops in the current-voltage characteristics of the  $P-N$  junctions if measured by an AC method. It is known that a high surface water content reduces the sensitivity of the surface recombination velocity to fluctuations of that content<sup>5</sup>). Consequently, we may expect the

curve of  $\alpha'$  as a function of vapour pressure, the temperature being constant, to gradually flatten out (fig. 3). This tendency will be enhanced by the fact that the recombination near the surface gradually loses its importance in relation to the other factors governing  $\alpha'$ , namely the recombination inside

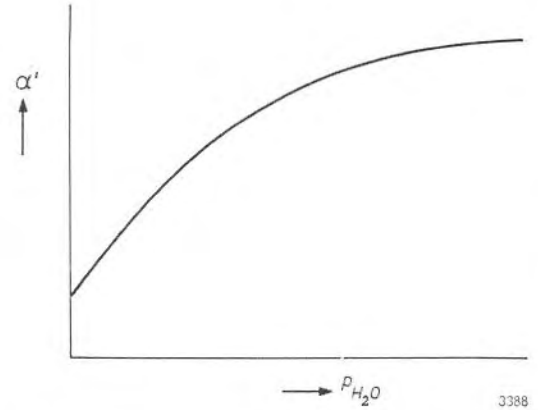


Fig. 3. Expected variation of current amplification factor  $\alpha'$  with water-vapour pressure  $p_{H_2O}$ , assuming constant temperature and equilibrium between  $p_{H_2O}$  and the surface occupation by water.

the base and the emitter loss. In general, a favourable surface water occupation is found in air of room temperature with a relative humidity in the region of 60%, the value of  $\alpha'$  then being high and little dependent on fluctuations of water-vapour pressure.

#### Stabilization with a water-vapour buffer

It follows from the foregoing considerations that a stable transistor can be obtained by introducing a "stabilizer" inside the encapsulating envelope, i.e. a substance that fixes the water-vapour pressure at a favourable value and thus acts in that respect as a buffer. The stabilizer must ensure a favourable water-vapour pressure at all temperatures which the transistor is likely to reach in normal operation: if the temperature rises, the water-vapour pressure will have to increase in such a way that the existing surface water occupation is maintained. In a graph of temperature  $t$  versus water-vapour pressure  $p_{H_2O}$  there will be a region of favourable combinations of  $t$  and  $p_{H_2O}$  as shown by the hatching in fig. 4. The water-vapour pressure of the stabilizer as a function of temperature is required to have a curve that lies within this region in the whole temperature interval of interest for the transistor.

Since, in principle, the surface occupation by water is kept constant under all conditions, inertia effects due to changes in surface water no longer occur.

<sup>4</sup>) J. T. Wallmark and R. R. Johnson, Influence of hydration-dehydration of the germanium oxide layer on the characteristics of  $P-N-P$  transistors, R. C. A. Review 13, 512-524, 1957; also A. J. Wahl and J. J. Kleimack, Factors affecting reliability of alloy junction transistors, Proc. Inst. Radio Engrs. 44, 494-502, 1956.

<sup>5</sup>) J. H. Forster and H. S. Veloric, Effect of variations in surface potential on junction characteristics, J. appl. Phys. 30, 906-914, 1959; also J. R. A. Beale, D. E. Thomas and T. B. Watkins, A method of studying surface barrier height changes on transistors, Proc. Phys. Soc. 72, 910-914, 1958, and G. Adam, Der Einfluss der Gasatmosphäre auf die Oberflächenrekombination bei Germanium, Z. Naturforschung 12a, 574-582, 1957.

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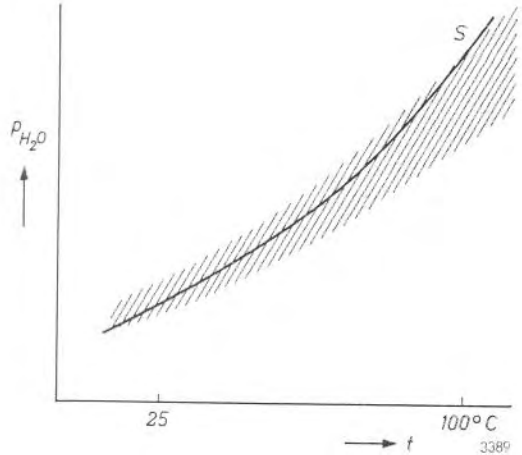


Fig. 4. Illustrating our picture of how the stabilization of transistors with the aid of a water-vapour buffer may occur. The temperature  $t$  is plotted versus the water-vapour pressure  $p_{H_2O}$  inside the transistor envelope. The hatched region comprises combination of  $t$  and  $p_{H_2O}$  that produce a favourable occupation of the transistor surface by water. The water-vapour pressure curve  $S$  of the stabilizing buffer should lie fully within the hatched region, for the temperature interval of interest.

Stabilization by "forming" the surface

In the following discussion of experiments it will be shown that reasonably stable transistors can be made with the aid of a water-vapour buffer. After prolonged tests, e.g. after some thousands of operating hours, however,  $\alpha'$  does usually begin to fall. This drawback can fortunately be overcome by slightly modifying the stabilizing method. A buffer is then used which, at room temperature, gives such a low water-vapour pressure that the surface water remains substantially below the region of favourable values ( $I$  in fig. 5). A transistor provided with such a buffer therefore has a low  $\alpha'$  until it has been sub-

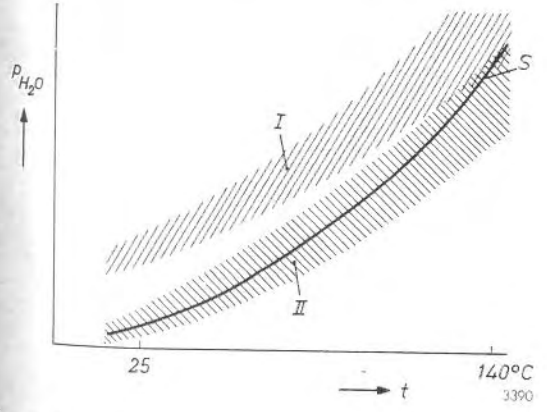


Fig. 5. Schematic representation of a working hypothesis concerning the stabilizing process where the surface of the transistor is "formed" with the aid of a buffer that gives a low water-vapour pressure.  $t$  temperature.  $p_{H_2O}$  water-vapour pressure. Curve  $S$  again represents the vapour pressure of the buffer. Region  $I$  covers the combinations of pressure and temperature that correspond to a favourable surface occupation by water before forming. After the forming process (prolonged heating at 140 °C) the favourable region corresponds to  $II$ .

jected to a special treatment. The latter consists of baking the transistor at 140 °C for several days. During the baking process something of the nature of surface "forming" takes place<sup>6)</sup>. Our hypothesis is that the region of favourable combinations of temperature and water-vapour pressure for the formed surface is now shifted so as to bring the  $p_{H_2O}$  curve for the buffer entirely into the favourable region (fig. 5).

Experiments

Drying of transistors

With the object of systematically investigating the influence of water vapour on transistors, a drying process was applied during which the change of  $\alpha'$  was followed. The transistors were dried both in vacuum and in air. For the vacuum drying the transistors are sealed into a relatively large glass tube (fig. 6). The lead-in wires are fused to the glass so far

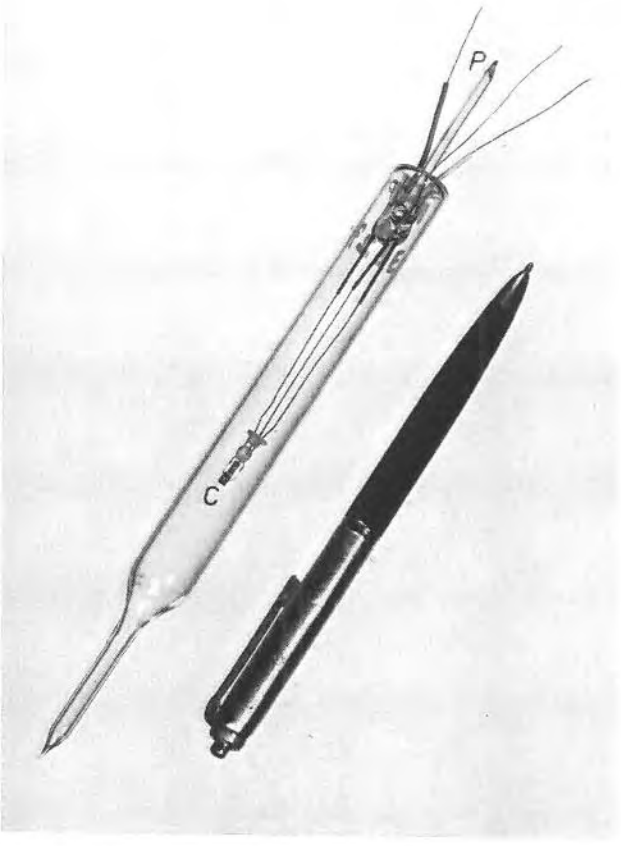


Fig. 6. In the water-vapour experiments the transistors were sealed inside glass tubes so designed that the temperature of the transistors is not significantly affected by the sealing operation. The transistor can be dried under vacuum.  $P$  is the pump stem,  $C$  the transistor.

<sup>6)</sup> J. T. Wallmark, Influence of surface oxidation on alpha c.b. of germanium P-N-P transistors, R.C.A. Review 18, 255-271, 1957.

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from the transistor that the transistor remains virtually unaffected. When the tube is now evacuated at room temperature,  $a'$  gradually falls, but so slowly that the final value is still not reached after days on the pump. Under these conditions the water bound to the germanium is released only very slowly. Evacuation at a higher temperature, e.g. at 100 °C, causes  $a'$  to drop faster, but here again, no final value is reached for several days. After pumping at 140 °C, however,  $a'$  generally drops in about six hours to a final value which is 10 to 15% of the initial value.

The rate at which  $a'$  decreases depends on the pre-treatment of the transistors, particularly on the etching. For example, transistors that have been electrolytically etched in KOH show a much faster drop upon evacuation than transistors that have been etched in acid. However, the final value reached by  $a'$  after prolonged pumping at high temperature is always just about as low, whatever the method of etching adopted.

The subsequent admission of a dry atmosphere, e.g. dry air, dry oxygen, or dry nitrogen, has no or scarcely any effect on  $a'$  even after long storage. The admission of a humid atmosphere, however, sends  $a'$  up again. Sometimes it may rise very rapidly, often increasing in one second by a factor of 5 to 10, sometimes back to its original value. The rate at which  $a'$  recovers depends, like the rate at which it falls, on the pre-treatment, that is on the method of etching and on the baking temperature. It depends, too, on the humidity of the air admitted. A relative humidity of 60 % is found to be most effective. After the first step rise, there is usually a slow increase to the final value.

The fact that the recovery of the transistor is attributable to the water vapour is confirmed by experiments where pure water vapour is admitted to transistors dried in a vacuum. They show that  $a'$  recovers in the same way as in humid air. The glass apparatus used for these experiments can be seen in fig. 7.

In the drying experiments in air the transistors were heated in a small oven to which air had free access. The behaviour of transistors dried in air is broadly the same as that of transistors dried in vacuum: during the drying process,  $a'$  falls at a rate depending on how high the temperature is. Here again,  $a'$  falls faster (though not lower) in transistors electrolytically etched in KOH than in acid-etched transistors. Usually the decrease does not continue so far as when the transistors are dried in vacuum, where the drying process is more rigorous. When the dried transistors are again exposed to moist

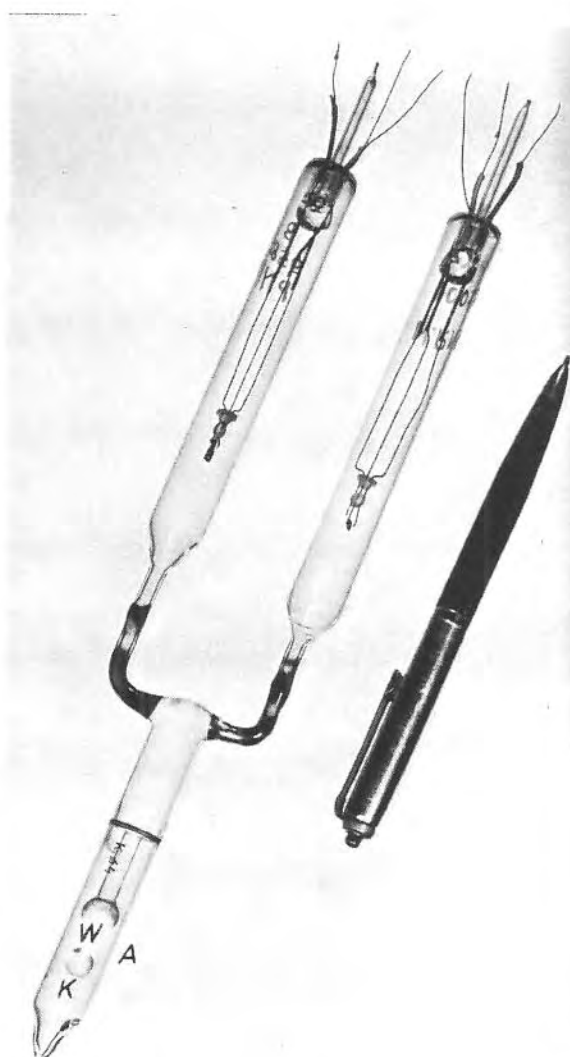


Fig. 7. Glass apparatus for admitting pure water vapour to vacuum-dried transistors. The marble *K* is used to break the spherical partition *W* which seals off the space *A* containing water. The water-vapour pressure is regulated by the temperature of space *A* (provided this temperature is lower than that of the space in which the transistor is situated). The apparatus here contains a *P-N-P* and an *N-P-N* transistor, for the purpose of comparing the behaviour of the two types.

air,  $a'$  again recovers, but normally at a much slower rate than after drying in vacuum. In every case it appears that the state of the surface (i.e. the degree of oxidation) does not affect the rule that a certain surface occupation by water is necessary to obtain a high  $a'$ , but the surface oxidation does affect certain details of the transistor's behaviour, as for example the rate with which the water makes its presence felt.

To check by other means whether the dehydration of the surface is in fact responsible for the decrease of  $a'$ , transistors were heated at 140 °C, the water-vapour pressure being increased to maintain a certain surface water occupation. It was found that,

under a water-vapour pressure of 300 to 400 mm Hg, the original values of  $\alpha'$  remain virtually unchanged.

*Stabilization experiments with a water-vapour buffer*

Transistors are frequently sealed into small glass envelopes. It can be seen in *fig. 8* that the dimensions of such an envelope are still considerable compared with the size of the crystal. If this were not so, the crystal would be too near the seal and would be overheated during the sealing operation. Further protection is afforded the crystal by filling the envelope with an appropriate substance. Silicone grease, such as used for high-vacuum purposes, is a suitable and widely used filler.

On page 206 it was argued that stable transistors may be expected if we introduce into the transistor enclosure a buffer which will keep the water-vapour pressure at a favourable value at any working temperature. A silicone grease which has absorbed some moisture, having for example been exposed for 24

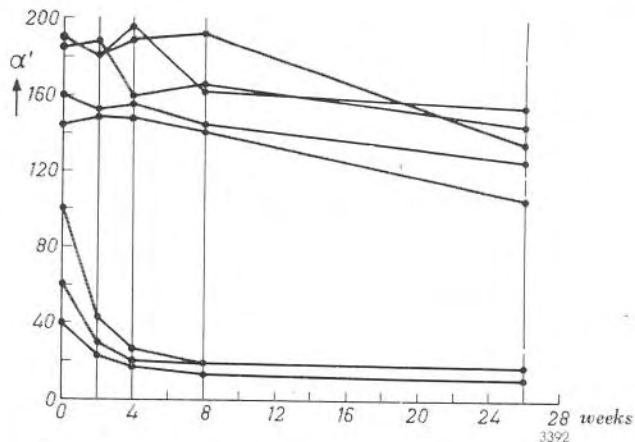


Fig. 9. Typical current amplification factor  $\alpha'$  versus time after encapsulation in dry silicone grease (lower three curves) and in moist silicone grease (upper five curves). The ambient temperature during the experiments was 50 °C, and 50 mW was dissipated in the transistors. The temperature of the germanium crystal was 85 °C. The transistors used were P-N-P types, electrolytically etched in KOH.  $\alpha'$  was measured at room temperature.

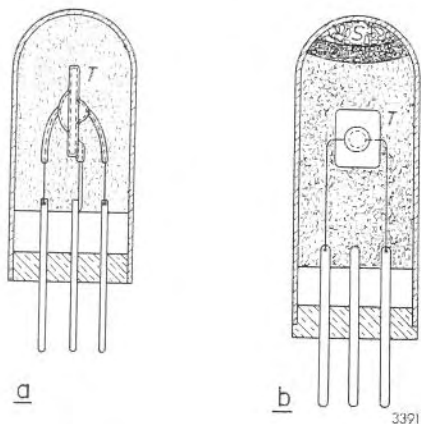


Fig. 8. a) Sketch of a transistor *T* in its envelope. The envelope is largely filled with a filler material (e.g. a silicone grease) to protect the germanium crystal during seal-off. b) The envelope here contains a buffer or stabilizer *S*, separated from the silicone grease by a porous plug. At all temperatures the buffer produces a water-vapour pressure which keeps the water content of the germanium surface constantly favourable.

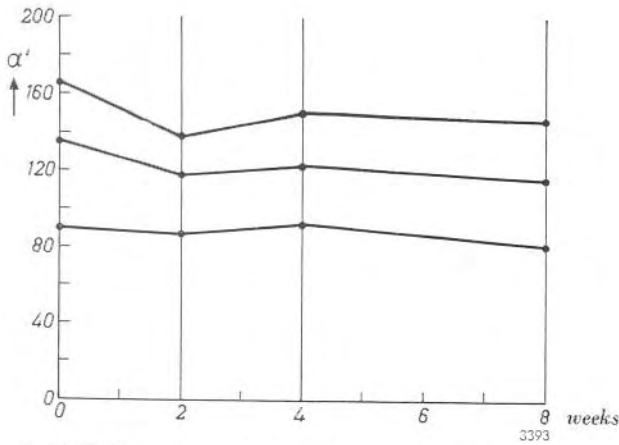
hours to air of 30% relative humidity, performs this function reasonably well. *Fig. 9* shows that transistors with a filling of *dry* silicone grease exhibit low values of  $\alpha'$  immediately after seal-off, which moreover drop appreciably in a few weeks. The same figure shows that, where a *moist* silicone grease is used,  $\alpha'$  is much higher and, what is more, fairly constant.

Numerous experiments were also done with transistors whose envelopes contained, in addition to the silicone grease, a substance separately introduced as a water-vapour buffer. The buffer was either kept

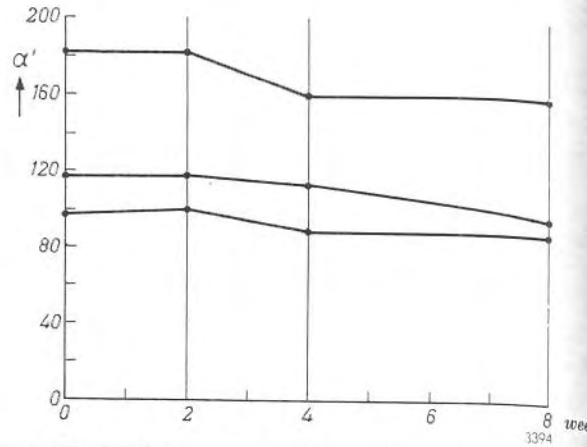
distinct from the grease by means of a porous plug (*fig. 8b*) or it was mixed with the grease. *Figs. 10a, b, c* and *d* give some examples of the favourable effect produced by some of these buffers (mentioned in the captions). The results in *figs. 10e* and *f* relate to transistors which contained, instead of a silicone grease, slightly moistened sand or silica gel, both of which substances serve the dual purpose of filler and buffer. These two examples support the hypothesis that the behaviour of the transistor is governed mainly by the moisture inside the enclosure, and not by the silicone grease or the combination of water and silicone grease.

In *fig. 10f* it is noticeable that  $\alpha'$  rises steeply during the first weeks, after which it remains roughly constant. We attribute this to the loss of water from the transistor surface when it is sealed into its envelope. Heat conduction through the electrodes then makes the crystal fairly hot, but the surroundings are kept cool, so that the water-vapour pressure remains low. After the seal-off, a low  $\alpha'$  may therefore be expected. The surface water occupation is now out of equilibrium with the vapour pressure produced by the buffer, but at room temperature the equilibrium is restored only very slowly. If the transistor is operated, its temperature rises and the return to equilibrium is accelerated, which is apparent from changes in  $\alpha'$ . If the transistor is kept at 100 °C,  $\alpha'$  usually reaches its stable value after a few days. The transistors to which *fig. 10f* relates were not subjected to this pre-heating.

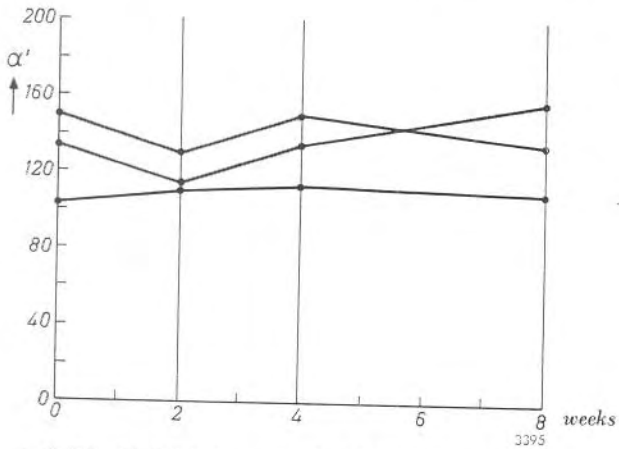
The temperature must not be raised above 100 °C with the object of speeding-up the above process. Experience has shown that higher temperatures, in conjunction with the high water-vapour pressure then produced by the buffers, inflict damage to the germanium surface, one result of which is a particularly low  $\alpha'$ . Re-etching is then the only way to save the transistor.



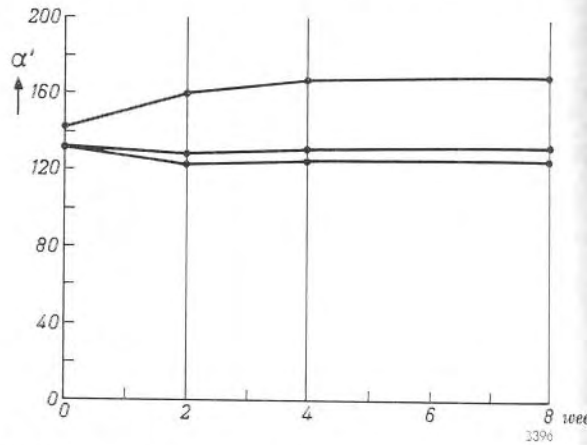
a)  $\text{BaCl}_2 \cdot 2\text{aq}$ , separated from silicone grease (cf. fig. 8b).



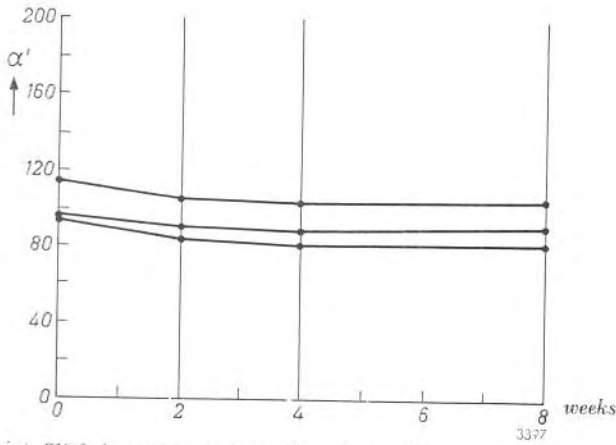
b)  $\text{K}_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{aq}$ , separated from silicone grease.



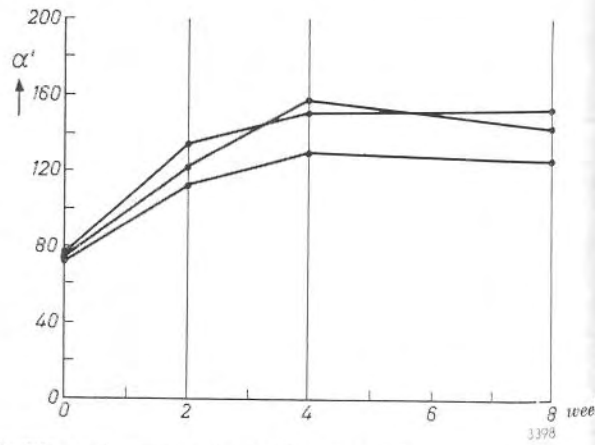
c)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{aq}$ , mixed with silicone grease.



d) Boracic acid, mixed with silicone grease.



e) Slightly moist sand, serving also as filler material.



f) Silica gel, serving also as filler material.

Fig. 10. Examples of the behaviour of transistors with a buffer incorporated in the encapsulant to stabilize the water-vapour pressure. Ambient temperature  $50^\circ\text{C}$ ; dissipation  $50\text{ mW}$ ; temperature of germanium crystal  $85^\circ\text{C}$ .  $\alpha'$  was measured at room temperature. The curves relate to *P-N-P* transistors, electrolytically etched in  $\text{KOH}$ . The buffer used is mentioned below each graph. The level of  $\alpha'$  is not characteristic of the buffer used.

*Stabilization experiments by "forming" the surface*

In order to stabilize transistors by "forming" their surface (p. 207), a buffer has to be introduced that gives a lower water-vapour pressure than is required for normal stabilizing. We have achieved successful

results with transistor fillings consisting of a silicone grease mixed with a little boracic acid (say 5% by weight), from which water is expelled to the required degree by drying. If the encapsulated transistors are formed by heating them for three days at  $140^\circ\text{C}$ .

stable transistors are produced which possess favourable properties in every respect. Fig. 11 demonstrates the stability of  $\alpha'$  after weeks of continuous loading; fig. 12 represents  $\alpha'$  as a function of the time of storage at 100 °C.

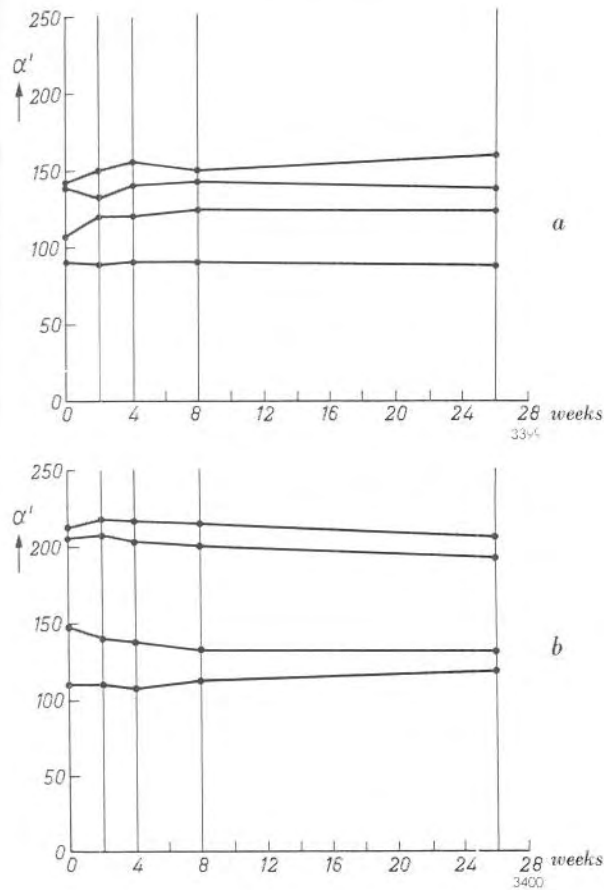


Fig. 11. Examples of the behaviour of  $\alpha'$  in life tests on transistors stabilized by surface forming at 140 °C. Buffer 5% pre-heated boracic acid, mixed with silicone grease. Dissipation 50 mW (5 mA, 10 V). Ambient temperature 50 °C, the temperature of the crystal then being 85 °C.  $\alpha'$  was measured at room temperature. (The level of  $\alpha'$  is not characteristic of the stabilizing method or of the type of transistor.)

a) P-N-P transistors.  
b) N-P-N transistors.

It is particularly important to extend the forming process over a sufficiently long period of time. It is seen from fig. 13 that  $\alpha'$ , as expected, is low immediately after encapsulation. After heating at 140 °C for one day, its value has increased considerably, but there is again a sharp drop after storing the transistor for a day at room temperature. The forming process was too short. After prolonged heating at 140 °C (here 6 days), however, the improvement achieved is not lost again. But the forming should not be too prolonged, otherwise  $\alpha'$  begins to fall once more.

Longer forming is required, or a higher forming temperature, the lower is the vapour-pressure curve of the buffer. This is illustrated in fig. 14, which relates to a transistor whose envelope was filled with a silicone grease mixed with boracic acid, which had been dried out more than in the cases earlier discussed. In practice the mixture of silicone grease and boracic acid will be chosen with a view to limiting the forming process to

a few days of heating at 140 °C. A higher temperature is undesirable, since the indium in the collector and emitter melts at about 155 °C.

It is likely that during the forming process — and perhaps afterwards — the silicone grease in combination with the boracic acid has its own advantageous effect. At the forming temperature there may well be reactions between the grease and the boron compounds which favourably influence the transistor's characteristics. However, that water vapour plays the major role in the forming process appears from the fact that transistors with very low values of  $\alpha'$  are obtained when a drying agent, e.g. barium oxide, is added inside the envelope.

The method of stabilization by forming the surface in a mixture of silicone grease and boracic acid not only produces high and stable values of  $\alpha'$ , but also benefits other important transistor characteristics (Table I). For example, the saturation leakage currents at the P-N junctions are small and do not drift. This is in contrast with the leakage currents in many commonly used transistors, which may gradually assume appreciable values, particularly if the temperature of the transistor is relatively

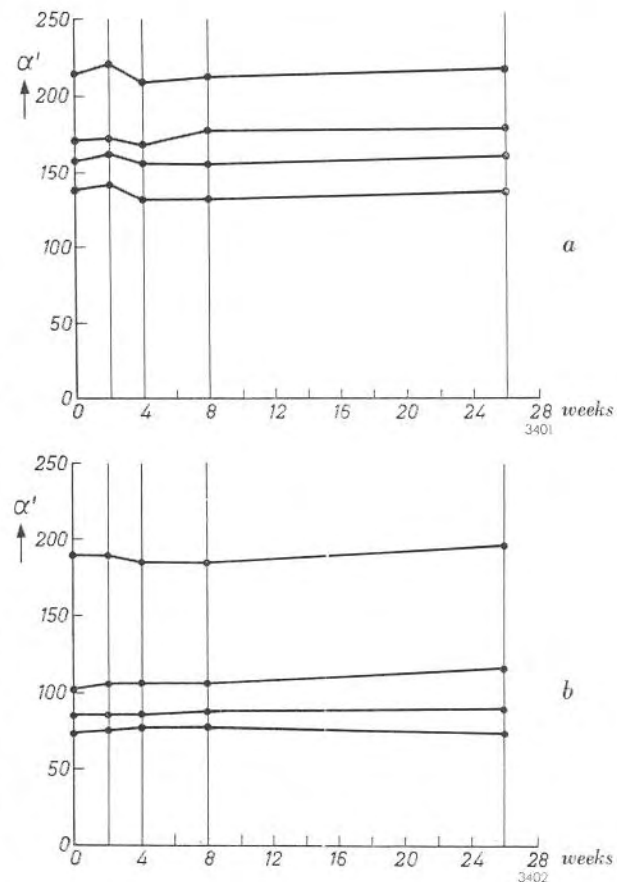


Fig. 12. Examples of the behaviour of  $\alpha'$  in storage tests at 100 °C on transistors stabilized by forming. Buffer 5% preheated boracic acid, mixed with silicone grease.  $\alpha'$  was measured at room temperature. (The level of  $\alpha'$  is not characteristic of the stabilizing method or of the type of transistor.)

a) P-N-P transistors.  
b) N-P-N transistors.



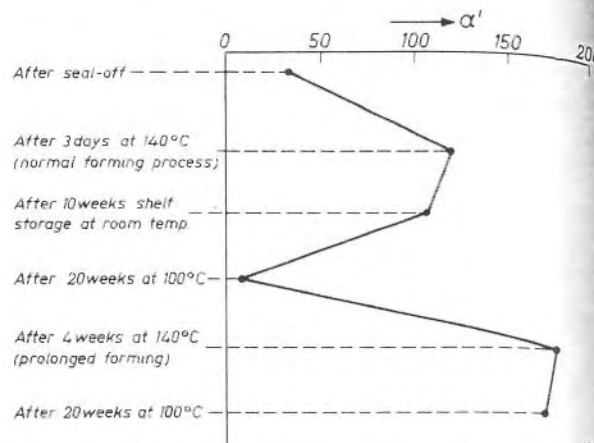
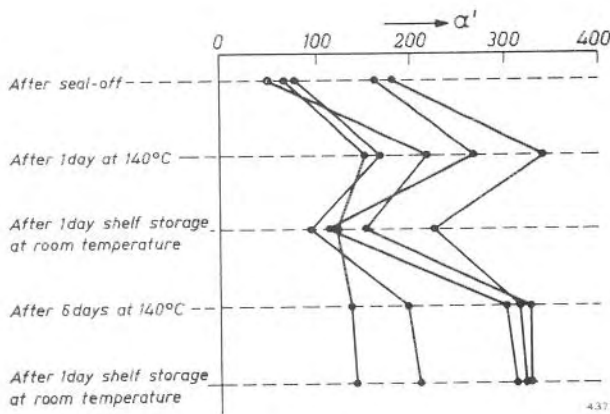


Fig. 13. Variation of  $\alpha'$  of some *P-N-P* transistors, electrolytically etched in KOH, which were initially formed for too short a time (one day) and subsequently for a long enough time (six days).  $\alpha'$  was measured at room temperature.

Fig. 14. Variation of  $\alpha'$  of a transistor formed with a buffer giving a considerably lower water-vapour pressure than in the cases to which figs. 11, 12 and 13, and Table I, refer.  $\alpha'$  was measured at room temperature.

**Table I.** The current amplification factor  $\alpha'$ , the saturation leakage currents  $I_{C0}$  at the collector junction and  $I_{E0}$  at the emitter junction, and the noise, of representative examples of *P-N-P* and *N-P-N* transistors, after various successive treatments. The transistor envelopes were filled with a silicone grease mixed with 5% boracic acid, dehydrated to a certain degree by pre-drying. The measurements were done at room temperature.

	<i>P-N-P</i>				<i>N-P-N</i>			
	$\alpha'$	$I_{C0}$ ( $\mu A$ )	$I_{E0}$ ( $\mu A$ )	Noise (dB)	$\alpha'$	$I_{C0}$ ( $\mu A$ )	$I_{E0}$ ( $\mu A$ )	Noise (dB)
After electrolytic etching in KOH	210	8	6	—	89	0.6	0.6	—
After seal-off	56	26	22	—	40	1.3	1.2	—
After 1 day at 100 °C	75	—	—	—	68	—	—	—
After 24 hrs storage at room temperature	60	2.8	2.7	4	53	4.4	3.5	6
After 3 days at 140 °C (forming)	158	—	—	—	164	—	—	—
After 24 hrs storage at room temperature	158	1.8	1.6	4	172	0.3	0.2	4

high (e.g. 60 °C). The table further shows that the noise level, which is often correlated with the leakage currents, is also favourable in formed transistors. In fact, the noise values found are just about the lowest yet measured on transistors.

In the case of *P-N-P* transistors the breakdown potentials of the two *P-N* junctions after forming are generally 20 to 30% lower than before. The breakdown potentials in *N-P-N* transistors are not significantly affected.

Finally it should be noted that surface forming also has a fairly marked influence on the  $I_E-V_{EB}$  characteristic (fig. 15).

**Stabilizing with arsenic**

Water is not alone in its property of reducing the recombination of holes and electrons at the germanium surface. Another substance with which we have successfully experimented is arsenic. At first sight there would seem to be no relation between water and arsenic, and the reader may well wonder

how it happened to be chosen for experiments at room temperature. It is not really so odd, however. Extensive physico-chemical investigations into the influence exerted by water on the surface of semiconductors have revealed that water adhering to such a surface tends to induce *N*-type surface conductivity. On *N*-type germanium, water thus makes the surface layer more strongly *N*-type than the interior, and on *P*-type germanium it makes the surface layer less strongly *P*-type than the interior. It may even result in the formation of an *N*-type surface layer on germanium that is otherwise weakly *P*-type<sup>7)</sup>. The question arose whether donor elements like arsenic, phosphorus, antimony and bismuth, with which germanium is doped, might induce *N*-type conductivity, might have a similar effect on the germanium surface as water has. This proved indeed to be the case, particularly as regards arsenic and phosphorus, which have measured vapour pressures at 140 °C.

<sup>7)</sup> R. H. Kingston, Water-vapor-induced *N*-type surface conductivity on *P*-type germanium, Phys. Rev. **98**, 1775, 1955.

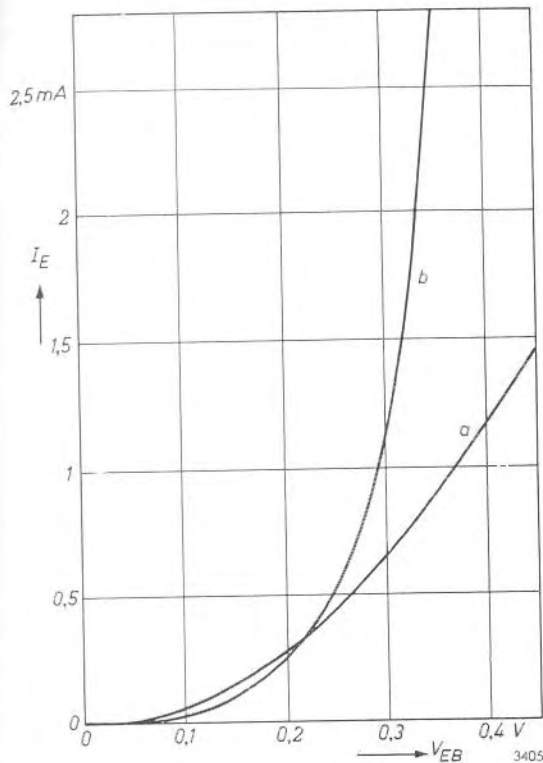


Fig. 15. Illustrating the effect of forming on the  $I_E$ - $V_{EB}$  characteristic of a P-N-P transistor; a) before forming, b) after forming.

We shall only comment briefly on the stabilizing method whereby a dried silicone grease mixed with a few percent by weight of arsenic powder is used as the filler substance in transistor envelopes. In its effect this mixture closely resembles the mixture of silicone grease and boracic acid used for the transistors stabilized by surface forming with water vapour. Again, a forming period of several days at 140 °C or higher is necessary. The resulting transistors have a high  $\alpha'$  and excellent stability (fig. 16). In fact, in many aging tests,  $\alpha'$  showed no change whatsoever.

It is not to be expected that the arsenic at 140 °C will really diffuse in the germanium surface layer and be incorporated in the germanium lattice as donor impurities normally are. For any significant diffusion to occur, the temperature would have to be at least 600 °C. Experiments have proved that the arsenic nevertheless gives rise to a surface layer which is strongly N-type. This layer persists as long as the transistor together with the arsenic is hermetically sealed. If the transistor is exposed to the ambient air, the surface layer changes and the transistor is no longer stable. The effect of the arsenic is entirely destroyed if the transistor is introduced into a space which is evacuated at high temperature. Evidently the arsenic is bound only very weakly to the germanium surface.

An advantage over the forming method using a silicone grease and boracic acid is that the transistors obtained are much more capable of withstanding high temperatures. Arsenically treated transistors can be held, for example, at a forming temperature of 140 °C for several months without deteriorating, whereas the same treatment with silicone grease and boracic acid would result in a considerable drop in  $\alpha'$ .

A complication is that transistors etched in KOH and subsequently formed with arsenic exhibit a marked "shelf after-effect". When such transistors, after a period of storage at room temperature, are raised to a higher temperature,  $\alpha'$  gradually rises for a few days. When the transistors are then returned to room temperature,  $\alpha'$  again declines, at

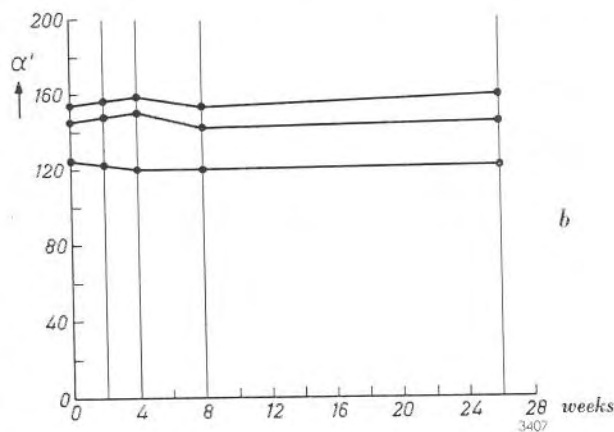
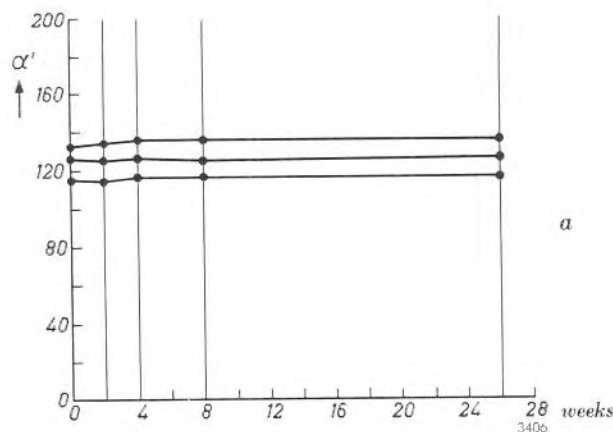


Fig. 16. Some examples of the constancy of  $\alpha'$  of transistors formed with arsenic. Before each measurement of  $\alpha'$ , the transistor was shelf-stored at room temperature for 24 hours. a) During operation; dissipation 50 mW, ambient temperature 50 °C. b) Stored, at 140 °C.

first rapidly and then slowly (fig. 17). It may be a month before the original value is reached. This effect is not found on transistors formed with a silicone grease and boracic acid mixture. The effect is apparently bound up with the presence of traces

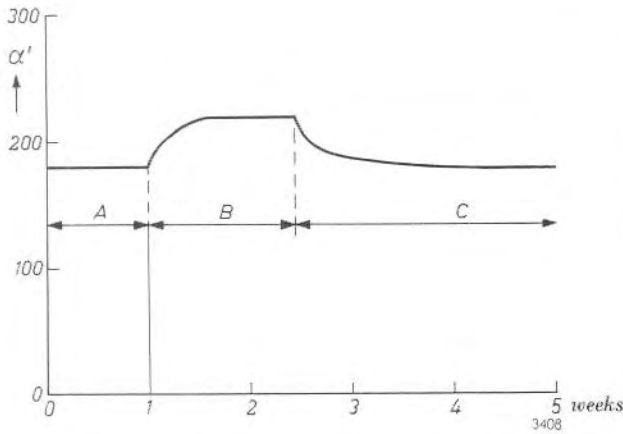


Fig. 17. Transistors formed at 140 °C, with powdered arsenic mixed in the silicone grease, often show a marked "shelf after-effect".

Period A: transistor at room temperature.  
 Period B: transistor at 100 °C.  
 Period C: transistor at room temperature.

of water in the transistor envelope, since if the transistors are rigorously dried after forming (by enclosing a drying agent in the envelope), the result is a high and stable  $\alpha'$  without this shelf after-effect.

A simpler way of eliminating the effect is to mix boracic acid as well as arsenic with the grease. This is the procedure with which we have so far achieved the best results. The transistors so treated combine the advantages of boracic-acid and arsenic forming namely no shelf after-effect, high and very constant value of  $\alpha'$  and high temperature stability.

**Summary.** The surface state of germanium transistors has a very marked influence on their characteristics, in particular on the current amplification factor. The occupation of the surface by water molecules is shown to be exceptionally important, and is thought to have an optimum value. A favourable water occupation may be maintained in all operating conditions by incorporating in the encapsulant a buffer substance — a stabilizer — which provides the appropriate water-vapour pressure as a function of temperature. Whilst this method produces good transistors with reasonably stable characteristics, better results are obtained with a buffer whose water-vapour pressure is initially too low. After the transistors have been heated for several days, they are then found to have very favourable and stable characteristics. The process is described as "surface forming". There are other substances that resemble water in their effect on the surface. Results obtained with one such substance (arsenic) are briefly discussed.

## ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS BY THE STAFF OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk \* can be obtained free of charge upon application to the Philips Research Laboratories, Eindhoven, Netherlands,

**2780:** S. Duinker: General energy relations for parametric amplifying devices (T. Ned. Radiogenootschap 24, 287-310, 1959, No. 5).

It is shown that the energy relations pertaining to parametric amplifying devices, as they have been derived by various authors, are a direct consequence of the invariance of the total-energy function of the parametric system under certain transformations. The theory is generalized so as to comprise arbitrary parametric systems. Some general properties of parametric systems, which can be deduced immediately from the energy relations, are discussed. A small number of typical examples are briefly treated to illustrate some fundamental principles following from the general theory.

**2781:** W. Albers and J. T. G. Overbeek: Stability of emulsions of water in oil, I. The correlation between electrokinetic potential and stability (J. Colloid Sci. 14, 501-509, 1959, No. 5).

Experiments on water-in-oil emulsions of moderate concentration, stabilized with oil-soluble,

ionizing stabilizers, show that in these emulsions no correlation exists between stability against flocculation and electrokinetic potential. Although according to theoretical calculations, energy barriers of over  $15 kT$  are present if the radius of the dispersed globules is about  $1 \mu$  and the electrokinetic potential exceeds 25 mV, they apparently do not prevent lasting contact between particles. All the emulsions flocculate rapidly, even in the presence of a surface potential considerably higher than 25 mV. A rather pronounced anticorrelation exists between the zeta potential and coalescence. It is explained as a consequence of the free mobility of the stabilizing molecules in the interface. The good stabilization against coalescence caused by some oleates of polyvalent metals is due to the formation of a thick film of partial hydrolyzates in the interface.

**2782:** W. Albers and J. T. G. Overbeek: Stability of emulsions of water in oil, II. Charge as a factor of stabilization against flocculation (J. Colloid Sci. 14, 510-518, 1959, No. 5).