INFLUENCE OF HYDRATION-DEHYDRATION OF THE GERMANIUM OXIDE LAYER ON THE CHARACTERISTICS OF P-N-P TRANSISTORS

By

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Summary—*It has been found that when germanium p-n-p transistors are subjected to a change in temperature, the current-transfer ratio, α_{fe}, shows a corresponding change, approaching an asymptotic value in approximately 48 hours. Simultaneously the saturation current of the emitter and collector junctions show a similar change. In this paper, this effect is interpreted in terms of a hydrated oxide layer on the germanium surface.*

The effect can be reduced either by minimizing the amount of water inside the transistor enclosure, or by using a drying agent (a getter) in the enclosure with a water retention that is considerably stronger than that of the germanium oxide layer.

Introduction

The influence of water vapor on the characteristics of the germanium surface has long been studied to obtain information about the surface layer and its effects on the stability characteristics of transistors. A review of such studies has been published by Kingston.[1] Even minute traces of water produce such large effects that hermetic encapsulation of transistors in a dry surrounding had to be introduced before their characteristics could be made reasonably stable.

As shown by Bardeen and Brattain,[2] and later elaborated by others,[3-5] water vapor introduces positive trapped charge on the ger-

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[1] R. H. Kingston, "Review of Germanium Surface Phenomena," *Jour. Appl. Phys.*, Vol. 27, p. 101, February, 1956.

[2] J. Bardeen and W. H. Brattain, "Surface Properties of Germanium," *Bell Sys. Tech. Jour.*, Vol. 32, p. 1, January, 1953.

[3] H. Statz, G. A. deMars, L. Davis and A. Adams, "Surface States on Silicon and Germanium Surfaces," *Phys. Rev.*, Vol. 101, p. 1272, February, 1956.

[4] R. H. Kingston, "Water-Vapor-Induced n-Type Surface Conductivity on p-Type Germanium," *Phys. Rev.*, Vol. 98, p. 1766, June, 1955.

[5] H. C. Montgomery and W. L. Brown, "Field-Induced Conductivity Changes in Germanium," *Phys. Rev.*, Vol. 103, p. 865, August, 1956.

manium surface, driving the surface conductivity towards n-type. This paper shows that at least part of this process has a long time constant (of the order of several hours). Because of the time required for the process to reach equilibrium, it has sometimes been called the "48-hour" effect. The effect is present in varying degrees in most commercial transistors. It shows up as a slow change in surface potential of the germanium surface, and therefore also in the current-transfer ratio and the saturation current, when the transistor is brought from one temperature to another.

Evidence is presented to support the view that the chemical change of the surface responsible for the change in surface potential is a chemical condensation (hydration–dehydration) of the hydrous germanium oxide layer on the surface. In this process the oxide layer, when subjected to a reduction in relative humidity, gives off water slowly. Thus, new bonds of the type Ge-O-Ge are formed leading to a reduction in the solubility of the oxide.

The 48-Hour Effect

It has been found that when germanium p-n-p transistors are life tested at elevated temperatures (e.g., 85°C), and at intervals are brought back to room temperature for routine measurements, the current-transfer ratio, α_{fe} (formerly called α_{cb}), shows a slow decline. A final value is apparently reached after some 48 hours. Simultaneous with the decrease in α_{fe} a corresponding increase is found in the saturation current for the emitter and collector junctions suggesting that the primary factor responsible for the change is the surface potential. Figure 1 shows results from measurements on a group of 18 germanium p-n-p transistors, hermetically encapsulated in dry air (Dew point −10° to −30°F) with a silicon resin covering the transistor surface. The transistors were life tested for 1,500 hours of shelf life at 85°C. At this point they were removed from the oven, cooled to room temperature and measured during storage at room temperature. The values of α_{fe} have been normalized to the initial reading taken 20 minutes after removal (which was chosen to allow temperature equilibrium to be reached). The decrease in α_{fe} after 48 hours amounts to nearly 20 per cent, although the value differs with the method of encapsulation as described later.

Since α_{fe} depends on several different factors, an independent test was made connecting the change to the surface recombination velocity, s, and thereby the surface potential. In this test a number of transistors were placed in an oven at 105°C for 25 hours, and then held at room temperature for an equal period. Measurements of α_{fe} at

room temperature were made at intervals. In the high temperature run the units were removed from the oven, cooled to room temperature, measured, and again placed in the oven. The results for a typical unit are shown in Figure 2. These results were analyzed according to the theory of Webster,[6] the details of which are given in Appendix I. The conclusion of this analysis is that the gradual change of the curves after subjecting the transistor to a new temperature can be accounted for by a change in s. Furthermore, relative values of s can be obtained with good approximation from the inverse of the measured values of α_{fe} at 1 milliampere emitter current.

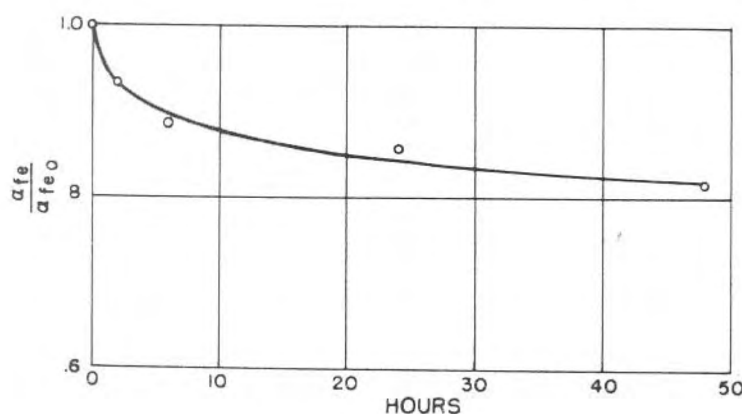

Fig. 1--The 48-hour effect. $\alpha_{fe}/(\alpha_{fe})_0$ versus time, where $(\alpha_{fe})_0$ is the value measured 20 minutes after removal of the units from the oven. Each point an average of 18 units.

That the 48-hour effect is entirely reversible is shown by the experimental results shown in Figure 2. Prior to the experiment the transistors had been aged at 105°C for a sufficient time so that the change in α_{fe} caused by oxidation[7] would be small and not interfere with the measurements. If this is not done the resulting α_{fe} will be a superposition of the two effects, namely the reversible change of the 48-hour effect and the nonreversible decrease caused by oxidation.

If the process responsible for the 48-hour effect is governed by an activation energy it would be expected that s should follow a logarithmic dependence of time. In Figure 3 the results of Figure 1 have been replotted in a semilogarithmic scale. Upper and lower quartile are shown. The straight line in Figure 3 represents the equation

[6] W. M. Webster, "On the Variation of Junction-Transistor Current-Amplification Factor with Emitter Current," *Proc. I.R.E.*, Vol. 42, p. 914, June, 1954.

[7] J. T. Wallmark, "Influence of Surface Oxidation on α_{cb} of Germanium p-n-p Transistors," *RCA Review*, Vol. XVIII, p. 255, June, 1957.

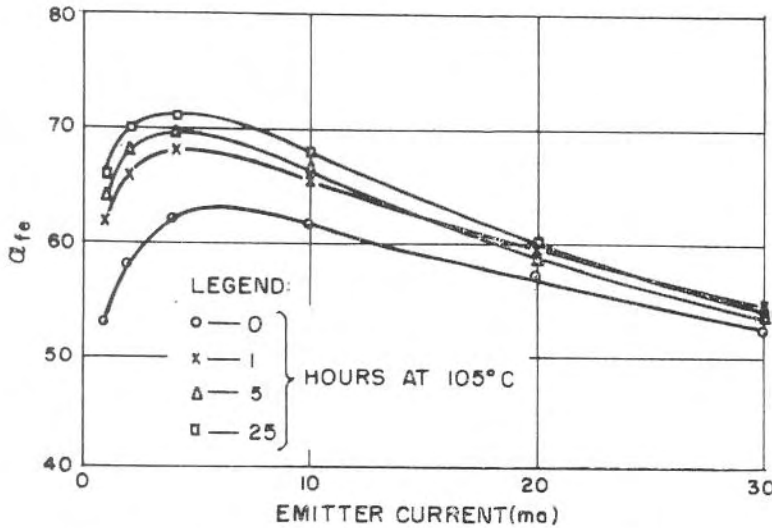

Fig. 2a—α_{fe} versus I_e for a unit stored at 105°C and measured at 25°C.

$$1/\alpha_{fe} = k_1 \log t + k_2, \tag{1}$$

which is the equation of a process governed by an activation energy. From the limited data of Figure 2 it appears that the activation energy is small, probably less than 3,000 calories per mole.

Influence of Oxide Thickness

Conceivably, the slow change found in the 48-hour effect might be connected to a transport time through the oxide layer on the germanium surface. Recently it has been shown that germanium oxidizes with a measurable rate even at room temperature.[7,8] Therefore, it

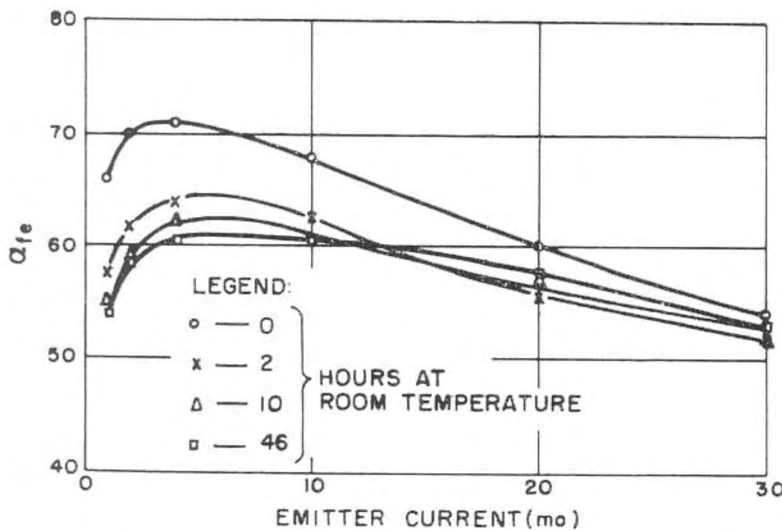

Fig. 2b—α_{fe} versus I_e for the same unit stored and measured at 25°C after the 105°C period.

[8] R. J. Archer, "Optical Measurement of Film Growth on Silicon and Germanium Surfaces in Room Air," *Jour. Electrochem. Soc.*, Vol. 104, p. 619, October, 1957.

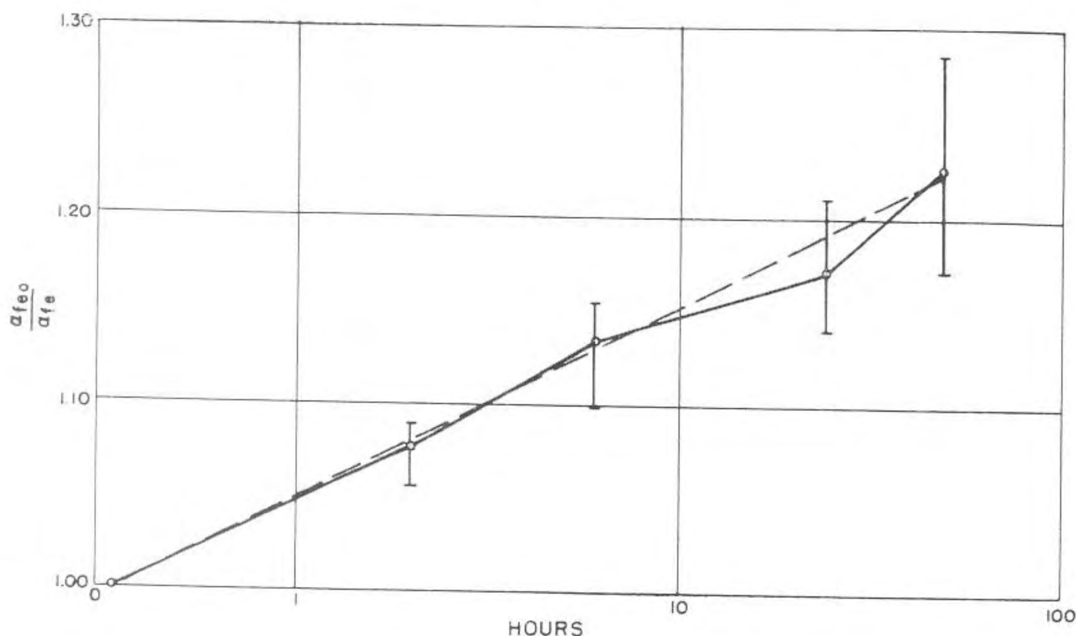

Fig. 3—Replot of the results in Figure 1 on a semilogarithmic scale. Each point an average of 18 units. Upper and lower quartile shown.

should be possible to measure the 48-hour effect on the same transistors early in life when the oxide thickness is small, and again late in life when the oxide layer has grown appreciably. Any difference in the characteristic decay time or magnitude of the effect could then be correlated with the oxide thickness. Figure 4 shows the results of such measurements in which the values of α_{fe} 48 hours after removal from an 85°C oven have been normalized to the values observed 20

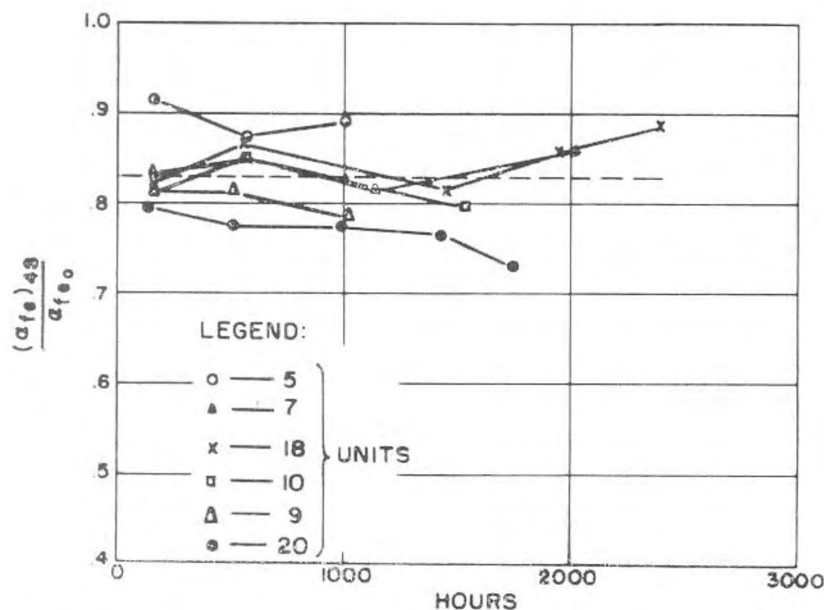

Fig. 4—The 48-hour effect at different stages of life. Each point an average of several units.

minutes after the removal. The measurements were made during several thousand hours of 85°C shelf life. During this time it is estimated that the oxide layer grew by approximately a factor of 4. However, no significant correlation between the amplitude of the 48-hour effect and the oxide thickness is apparent.

Figure 5 shows measurements similar to those of Figure 3 which were made during the life of a group of 7 transistors. No significant correlation can be found for the characteristic decay time derived from these results and the oxide layer thickness.

It is concluded, then, that the characteristic decay time of the 48-hour effect is not dependent on a transport process through the oxide layer.

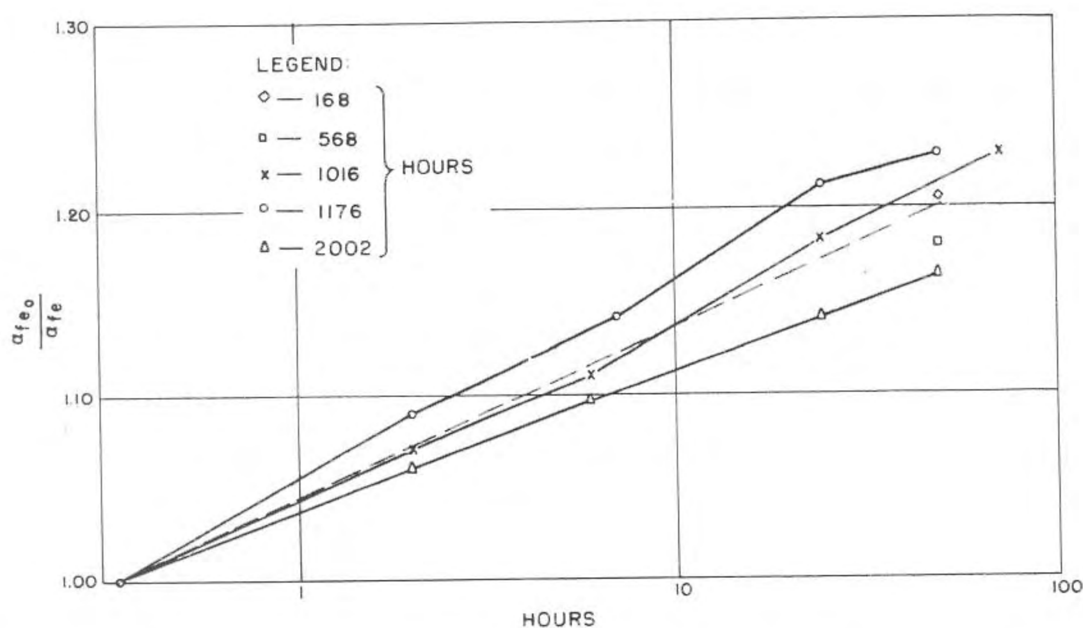

Fig. 5—One of the runs of Figure 4 plotted on a semilogarithmic scale.

Furthermore the independence of oxide thickness is hard to associate with a surface (of the oxide layer) phenomenon which definitely should decrease in amplitude as the oxide grows.

Influence of the Dryness of the Encapsulant

Experiments with different encapsulants revealed that the water retention capabilities and the dryness of the encapsulant had an influence on the amplitude of the 48-hour effect. Figure 6 shows results for units encapsulated in a vacuum of 10^{-4} mm Hg after baking in a vacuum of 0.5 mm Hg at 90°C for 6 hours. In this case the 48-hour effect amounts to only 3 per cent.

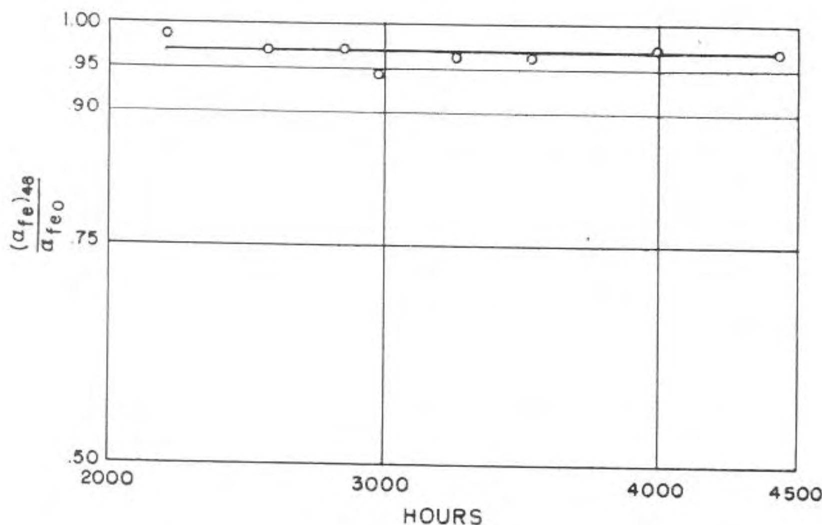

Fig. 6—The 48-hour effect for units encapsulated in a vacuum of 10^{-4} mm Hg. Each point an average of 5 units.

Figure 7 shows results for units encapsulated in a metal can containing molecular sieve (sodium and calcium alumino-silicates), prebaked to 220°C for 16 hours. Again the 48-hour effect amounts to only 3 per cent.

It is believed that the first of these tests corresponds to conditions of extreme dryness mentioned previously, while the second test exemplifies an encapsulant with high water retention capabilities.

These experiments suggest that minute amounts of water in the can (50 parts of water per million parts of encapsulant) are responsible for the effect. The results suggest that the germanium oxide layer has a water retention that is less than that of molecular sieve but larger than, or comparable to, that of the silicon resin encapsulant used in the tests shown in Figures 1-5.

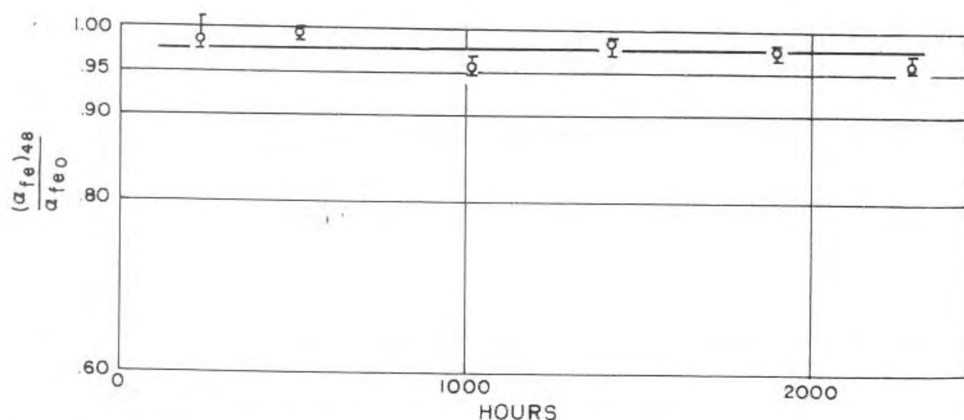

Fig. 7—The 48-hour effect for units encapsulated with dry molecular sieve. Each point an average of 19 units.

Solubility Measurements

An important clue to the nature of the 48-hour effect is the fact that the solubility of the oxide layer changes with heat treatment. More specifically the oxide layer when heated in a dry atmosphere becomes gradually insoluble in dilute NaOH at a rate that matches the rate of change of α_{fe}. Measurements of this effect were made in the following way. Samples of 8 ohm-centimeter n-type germanium were heated to 105°C for various lengths of time in air with a relative humidity of approximately 2 per cent. Thereafter the samples were washed in dilute NaOH to remove the oxide layer. The solution was evaporated to dryness and the residue was analyzed quantitatively in a spectrograph for germanium content. The details of the procedure will be published separately. The results are shown in Figure 8. Results for 100 per cent relative humidity are also shown in Figure 8 as a dashed curve. These results[7] were obtained at 85°C and extrapolated to 105°C.

The interpretation of these results suggests the presence of two competing processes. One is a straight oxidation process as found from the high relative humidity experiments. The other is a gradual decrease in the solubility of the oxide layer as found in the low relative humidity experiment. The solubility decrease, therefore, must be related to the loss of water from the oxide layer at low relative humidities. To develop a quantitative expression for these processes, let us assume that the oxidation rate is not too different at high and low relative humidities. This assumption is supported by the nearly identical initial rise of the two curves. Assume further that a simple energy activated process following the Elovich equation for the loss of water. Then the following differential equation governs the increase in soluble oxide:

$$\frac{dx}{dt} = \frac{Lt^{-2/3}}{3} - \frac{M}{t + t_0}, \qquad (2)$$

where x is the soluble oxide weight, and L and M are constants.

Fitting Equation (2) to the experimental results in Figure 8 we obtain quantitative expressions for the two processes taken separately. The expression for the growth of total oxide weight matching the dashed curve in Figure 8 is

$$x_{\text{ox}} = 4.9t^{1/3}. \qquad (3)$$

Similarly, the growth of insoluble oxide weight derived from matching the solid curve of Figure 8 with Equation (2) is

$$x_{\text{insol}} = 16 \log (t + 4.9) + N. \tag{4}$$

The conclusion derived from this experiment is that the drying-out process of the oxide layer as expressed in Equation (4) has a time dependence that agrees well with the 48-hour effect.

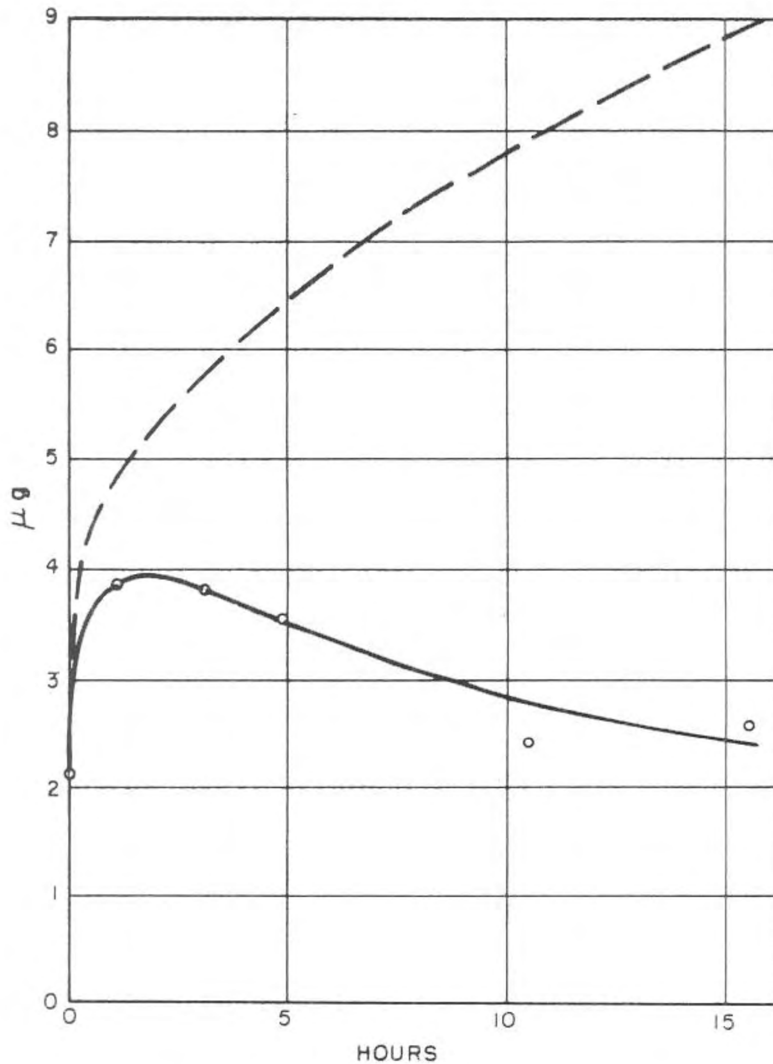

Fig. 8—Amount of oxide soluble in 5 minutes in 0.25 normal NaOH after oxidation in room air at 105°C.

Phenomenological Model of the Surface

In order to account for the observed behavior of the surface, the following model is presented. It is known that the germanium surface in a transistor is covered by a layer of oxide of a thickness of approximately 10-20 monolayers.[7,8] This oxide is soluble in H_2O, NaOH, and HF, and therefore has been assumed to consist of germanium dioxide.

The oxide layer is probably not crystalline as evidenced by X-ray investigations.[9] Initially the oxide layer is formed in an electrolyte such as KOH, and subsequently washed in H_2O. Therefore it has been suggested that the oxide contains OH-groups,[10] and possibly other groups, depending upon the chemical history of the unit. In the case of silicon, such a hydrous, noncrystalline silicon oxide (silica gel) is well known. As shown below, the picture of a hydrous germanium oxide in the form of a glassy or polymorphous substance, in analogy with silica gel containing a variable amount of water, fits the experimental data very well.

It is well known that silica gel, which may be thought of as a mixture of different silicic acids, gives off water through chemical

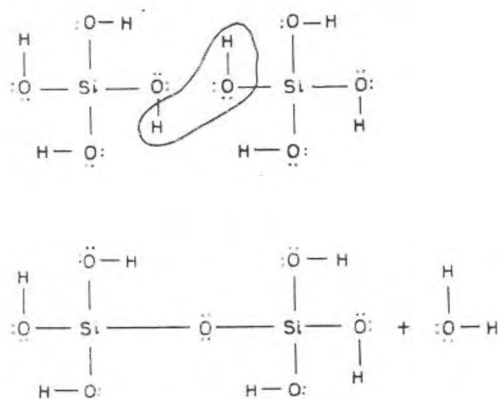

Fig. 9—The process of condensation. Two molecules disilicic acid form one molecule of metasilicic acid giving off one molecule of water.

condensation. In this process simple silicic acids form irregular Si–O–Si bonds, transforming to higher silicic acids as shown in Figure 9 for the transition of disilicic acid to metasilicic acid. The metasilicic acid in turn may condense further by combining with other acid molecules. This process is reversible with relative humidity, as is well known from the practical utilization of silica gel as a drying agent. What has been said here about silicon is true also about germanium (and other elements as well). Such a process would introduce irregular cross-links creating a glass-like structure without crystalline regularity. The solubility of such a structure would decrease markedly with amount of cross-linkage.

The hydration of the oxide layer introduces positive trapped charge, most likely one positive charge per broken cross-link. It is interesting

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[9] R. D. Heidenreich, as reported in Reference (2).

[10] D. R. Turner, "The Anode Behavior of Germanium in Aqueous Solutions," *Jour. Electrochem. Soc.*, Vol. 103, p. 252, April, 1956.

in this connection that OH— groups have been suggested as donors in oxide cathode coatings.[11] The positive charge constitutes a slow trap which according to the model is located in the oxide layer, and not only on the surface as has sometimes been assumed. However, the number of slow traps originated by the hydration is small, one or two orders of magnitude smaller than the number of slow traps originated by oxidation. When a germanium transistor is heated to an elevated temperature, water is given off from the interior of the can, from the encapsulants, and from the germanium oxide layer. If the water retention of the germanium oxide is larger than that of its surrounding, the equilibrium will be shifted to a stable state in which more water is found in the germanium oxide layer. This process will proceed at a rate that is governed by the activation energy of the absorption of water in the oxide, assuming that diffusion through the oxide is fast and therefore not rate determining. When the transistor is cooled down again the water equilibrium will shift back to its original state at a slightly slower rate, as the temperature is lower.

Discussion of Results

A considerable amount of data exists on the surface traps, their number, energy levels, etc. However, before the chemical–physical nature of the traps is known, it is difficult to design surface characteristics for specific device requirements. This paper points out the connection between the chemical nature of an important species of slow traps and the resulting surface potential.

Some practical consequences of the effect described are evident in the measurements of transistor characteristics. When a transistor has been removed from operation at a temperature above the ambient, the characteristics of the transistor will drift for some 48 hours until the change becomes imperceptible. This is especially true in life testing transistors, an operation which is often carried out at close to the rated maximum temperature. If the time between removal of the transistor from the high temperature and the subsequent measurement is not controlled, the measured values of α_{fe} and saturation current will show considerable spread, making rapid and reliable interpretation of trends difficult.

Another easily overlooked consequence is that the initial measurements on the transistor before the life test and the subsequent measurements during life are not comparable unless allowance is made for

[11] R. H. Plumlee, "Electron Donor Centers in the Oxide Cathode," *RCA Review*, Vol. XVII, p. 231, June, 1956.

the 48-hour effect. If this effect is not taken into account, the subsequent measurements of α_{fe} (and saturation current) will represent non-equilibrium values which are too high (or low). The usual drop in α_{fe} after the initial measurement, caused by progressive oxidation, is thereby masked, giving a false impression of stability.

There are two possible ways of reducing the 48-hour effect. One is the meticulous removal of moisture from the encapsulation and the transistor, heating the transistor for several hours at a temperature higher than the rated temperature. Another method is to employ a gettering agent with a water retention which is higher than that of the germanium oxide layer even at elevated temperatures. In a practical process, a combination of the two methods may offer advantages.

As an interesting by-product of the results, the magnitude of the 48-hour effect may offer an extremely sensitive and reliable method of testing the hermetic enclosure of transistors for leaks. In this application the 48-hour effect is considerably more sensitive than the conventional method of waiting for the reverse current–voltage characteristic to deteriorate.

Acknowledgment

It is a pleasure to acknowledge helpful discussions with E. L. Jordan, R. H. Plumlee, H. M. Pollack, L. R. Shardlow, and W. M. Webster, assistance with the spectrographic method by M. C. Gardels and H. M. Whitaker, and assistance with some of the measurements by R. R. Vannozzi.

Appendix

As shown by Webster[6]

$$1/\alpha_{fe} = Psg(z) + Q(1+z), \tag{5}$$

$$z = KI_e, \tag{6}$$

where Q and K are factors that depend on transistor dimensions and $g(z)$ is a field factor. P is a factor containing the effective area A_s in which surface recombination takes place. This area is given by

$$A_s = \frac{\pi}{4}(d_c^2 - d_e^2) + 2\frac{\pi}{4}[(d_c + L)^2 - d_c^2], \tag{7}$$

where

$$L = (D_p \, \tau_{eff})^{1/2}. \tag{8}$$

For $d_e = 0.015$ inch, $d_c = 0.045$ inch, and $\tau_{eff} < 15$ microseconds, Equation (7) becomes

$$A_s \approx \frac{\pi}{4} d_c^2 \, (1 + 4\, L/d_c). \tag{9}$$

For surface recombination dominating over bulk recombination,

$$\tau_{eff} \approx M/s. \tag{10}$$

where M is a proportionality constant. Therefore,

$$A_s \approx \frac{\pi}{4} d_c^2 \left[1 + \frac{4}{d_c} \left(\frac{D_p M}{s} \right) \right]^{1/2}. \tag{11}$$

Equation (11) represents a very slowly varying function of s. Furthermore, for relatively small changes in s, the variation of A_s can be accounted for by a somewhat reduced value of M, which can be determined from experiments. It will be assumed therefore that all terms in Equations (5) and (6) are independent of s, except s itself.

Fitting Equations (5) and (6) to the initial curve in Figure 2, one obtains

$$Ps = 4.0,$$
$$Q = 0.032,$$
$$K = 1.0 \text{ ma}^{-1}.$$

From these values it is clear that the influence on α_{fe} of the second term in Equation (5) measured at 1 milliampere emitter current is less than 2 per cent. As the total change in α_{fe} at the same current is approximately 20 per cent, the second term can be neglected. Therefore at 1 milliampere

$$1/\alpha_{fe} \propto s.$$