

LB-1073

INFLUENCE OF SURFACE

OXIDATION ON a_{cb} OF

GERMANIUM p-n-p TRANSISTORS

RADIO CORPORATION OF AMERICA
RCA LABORATORIES
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Approved

A handwritten signature in dark ink, appearing to read "Stuart W. Seely", is written over a horizontal line.

Oxidation of the surface of a germanium p-n-p transistor is shown to be a major factor influencing surface recombination and thereby the current transfer ratio, α_{cb} . When the transistor is electrolytically etched in potassium hydroxide, the surface becomes covered with a hydrated germanium monoxide-dioxide layer giving low surface recombination and high α_{cb} . During the subsequent life of the transistor, this layer grows through further oxidation, causing a reduction in α_{cb} . Since the rate of oxidation increases with temperature, and is initially quite high, slowing down with time, it has been advantageous in manufacturing to subject new transistors to heat treatment. This creates a specific thickness of oxide which during the subsequent life of the transistor does not change rapidly even at elevated temperatures.

Introduction

Drift of the electrical characteristics of transistors, especially of the current transfer ratio, α_{cb} , has long been a major problem in transistor applications. It has been known for some time that this drift is connected with changes in surface conditions.¹

The oxidation of the germanium surface is shown in this bulletin to be a major factor in the slow decay of α_{cb} in p-n-p transistors. The rate of decay increases with temperature and α_{cb} may change to such an extent that transistor circuits designed around the initial value of α_{cb} fail to operate properly after a period of time. Our knowledge of the oxidation of germanium is still somewhat incomplete, but, with the help of recent information, an outline of the processes responsible for this behavior may be sketched.

Evidence is presented to show that n-type germanium electrolytically etched in potassium hydroxide has a low surface recombination velocity, a high α_{cb} , and is covered by a thin germanium monoxide layer. The surface layer oxidizes further at temperatures between 25 degrees C and 125 degrees C according to the so called "cubic" law as is also the case with copper. This oxidation is in the form of a germanium dioxide layer whose growth is responsible for an increase in the surface recombination velocity and thereby a decay in the current transfer ratio.

Earlier Work on Atomically Clean Surfaces

On a freshly cleaved germanium surface, Green and Kafalas² have shown that at temperatures between minus

68 degrees C and plus 25 degrees C, chemisorption in less than five seconds covers the surface with about three oxygen atoms per surface germanium atom, thus building up first a very thin oxide layer. From then on the further chemisorption follows a logarithmic law,³

$$N = C_1 \log_{10} t + C_2, \quad (1)$$

where N is the number of oxygen atoms absorbed per cm^2 ,

t is the time in minutes,

$$C_1 = 1.4 \times 10^{14},$$

$$C_2 = 8.4 \times 10^{14}.$$

Both the p-type and n-type germanium obeyed a logarithmic law which could be observed for about 22 days until the rate was too small to measure.

At 500 degrees C, it has been shown by Law and Meigs⁴ that oxidation follows the parabolic law,

$$N = C_3 \times t^{1/2} \quad (2)$$

$$\text{where } C_3 = 9 \times 10^{13} \times p^{1/2}$$

p is the oxygen pressure,

and t is time in seconds.

This is typical of a process where diffusion through the formed oxide layer is the rate determining factor. At still higher temperatures, Law and Meigs,⁴ Bernstein and Cubicciotti,⁵ report a linear law in which the rate determining factor is the evaporation of germanium monoxide from the surface. This relation is given by,

$$N = C_4 \times t, \quad (3)$$

where C_4 is a pressure dependent factor.

Earlier Work on "Real" Surfaces

While the previously mentioned results are applicable to surfaces in contact with oxygen alone, it is obvious that etches commonly used to clean the germanium surface will lead to chemisorption of the etch constituents so that we are dealing with contaminated surfaces. On such a surface the contamination may significantly change the rate of further oxidation in a manner well known from oxidation studies⁶ once the germanium has been removed from the etching solution. Furthermore, as most germanium etches are oxidizing agents, they will leave an initial thickness of oxide on the surface. Green

and Smythe⁷ found that an etched surface may be covered by three monolayers of oxide five minutes after etching, increasing to six monolayers after three days exposure to room air. Contaminated surfaces are presently less understood than clean surfaces, and the considerable amount of data that exists on surface traps has yet to be interpreted and correlated with the chemical and physical processes that undoubtedly are responsible for the traps. The present bulletin constitutes a step in this direction.

Two Basic Surface Treatments

The results of two now well-investigated surface treatments for germanium are taken as a starting point. These results are used to form an hypothesis about the oxidation of germanium. This hypothesis is checked against the behavior of germanium transistors on life test. The two surface treatments are the so-called No. 5 etch and anodic oxidation in glacial acetic acid. The No. 5 etch⁸ is known to leave germanium monoxide, GeO , on the germanium surface, thereby making the surface conductivity strongly n-type. This gives p-n-p transistors a low surface recombination velocity and consequently a high α_{cb} and a low saturation current.

The anodic oxidation treatment⁹ in acetic acid is known to leave a layer of germanium dioxide, GeO_2 , on the surface. This dioxide layer affects the surface conductivity by changing it from n-type towards less n-type as shown by the results of the following experiment. Four groups of p-n-p transistors were etched electrolytically in potassium hydroxide and subsequently two of the groups were given the anodic oxidation treatment. Thereafter all groups were put on 85 degrees C shelf life test. In Fig. 1 is plotted α_{cb} (in percent of the initial value after the electrolytic etch) versus time. The solid line is the theoretical curve of Eq. 10 which is developed later in this paper. Each experimental point is an average of three units. As can be seen in Fig. 1 the untreated control groups behave quite normally, the experimental points falling near the theoretical curve. The oxidized groups

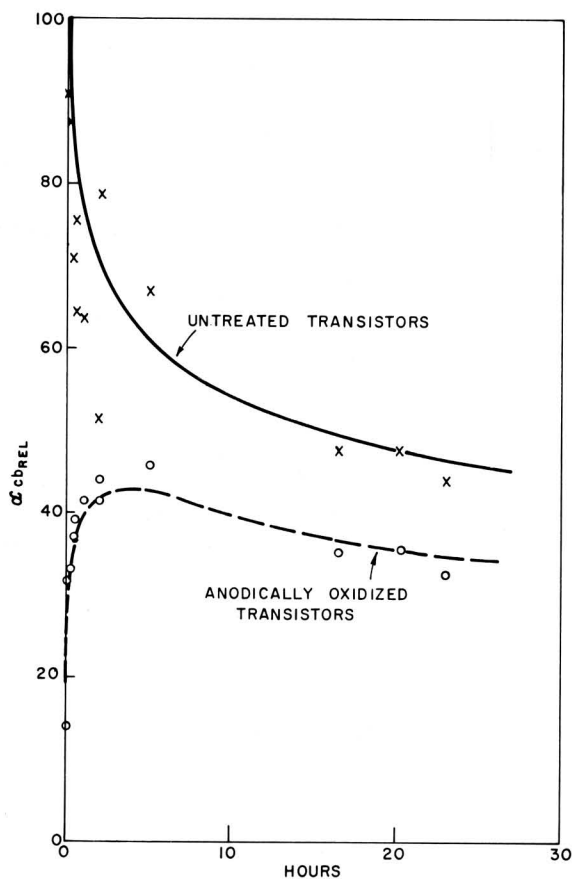


Fig. 1 - Influence on transistors of anodic oxidation in glacial acetic acid plus sodium acetate.

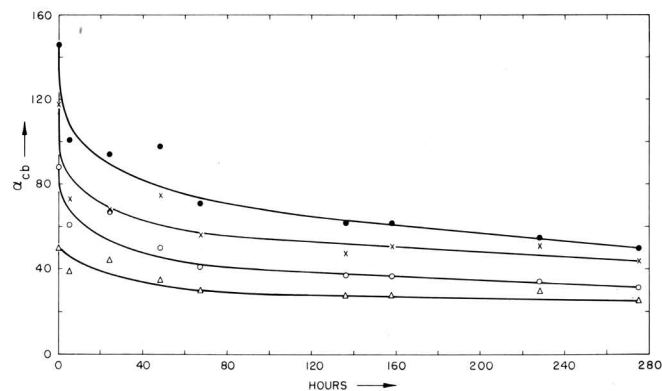


Fig. 2 - Life test results for encapsulated silicone-covered p-n-p germanium transistors. Shelf life at 70°C. (F. L. Hunter)

first show very low a_{cb} which, however, climbs rapidly (removal of bound etch constituents) and approaches a curve similar to the solid curve but shifted to the left. In other words, the oxidation treatment has applied an oxide layer of the same thickness as would be applied by heating to 85 degrees C for some 30 hours.

The terms GeO and GeO₂ have been used loosely as it is known that these oxides under the prevalent conditions take up a rather indefinite amount of H₂O forming various hydrated forms such as di- or metagermanic acids, etc.¹⁰ For silicon, which behaves in a similar manner, these processes have been studied, but for germanium the details are not as well known. Therefore the terms monoxide, GeO, and dioxide, GeO₂, have been used for simplicity without specifying the degree of hydration or atomic arrangement.

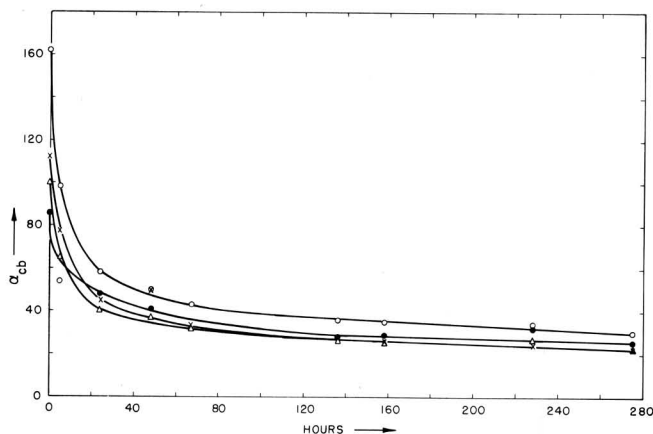


Fig. 3 - Shelf life at 85°C.

Without offering further proof at this time, it will be assumed now that similar oxidation processes take place during the conventional processing of transistors. In particular, it will be assumed that the high a_{cb} found in p-n-p transistors after an electrolytic etch in potassium hydroxide is a result of a layer of GeO on the surface of the germanium. The subsequent decay of a_{cb} may be interpreted as due to a growing layer of GeO₂ on top of the GeO layer. In line with this it has been found that a germanium surface freshly etched electrolytically in potassium hydroxide is n-type but in the course of many hours gradually becomes less n-type.¹¹

Experimental Results

The experimental part of this report consists of a number of life tests on transistors, comprising measurements of a_{cb} versus time under different conditions of test.¹²

It may be pointed out here that these data should not be interpreted as the performance of commercially available transistors. Factory procedures generally include an "aging" step, e.g. heating to an elevated temperature for a period of time. This reduces a_{cb} to approximately 35 percent of its original value, after which moderate temperatures within the rating of the transistor do not cause significant further changes. Thus commercial processes employ in some degree an oxidation process to achieve stability.

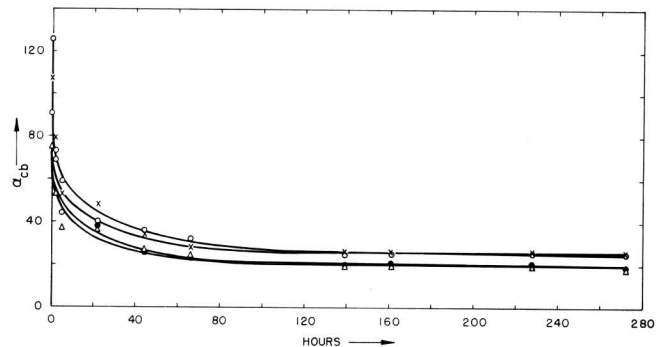


Fig. 4 - Shelf life at 105°C.

Life test data for four groups of p-n-p germanium transistors at four different temperatures are presented in Figs. 2 to 5. In each group there is one transistor for which a_{cb} seems to decay somewhat differently from the other three, perhaps because of a slight error in the initial a_{cb} reading. Therefore, an average has been taken of the three similar units, disregarding the fourth. In order to let all transistors contribute equally to the average, relative values have been used, setting the initial relative $a_{cb} = 100$. The results are shown in Fig. 8. For each point, the spread between the three values is shown. The transistors had been electrolytically etched in potassium hydroxide and hermetically encapsulated with a silicone resin covering the germanium surface.

Other runs were made in which it was established that the effect of embedding the transistor in silicone was inconsequential and that units in silicone or air

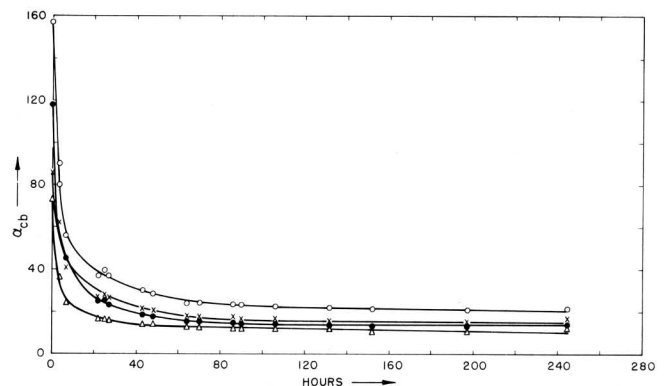


Fig. 5 - Shelf life at 125°C.

showed identical behavior within the accuracy of measurement. Vacuum sealed (10^{-4} mm Hg) units showed reduced decay as shown in Fig. 6. This is to be expected if the decay is caused by an oxidation process.

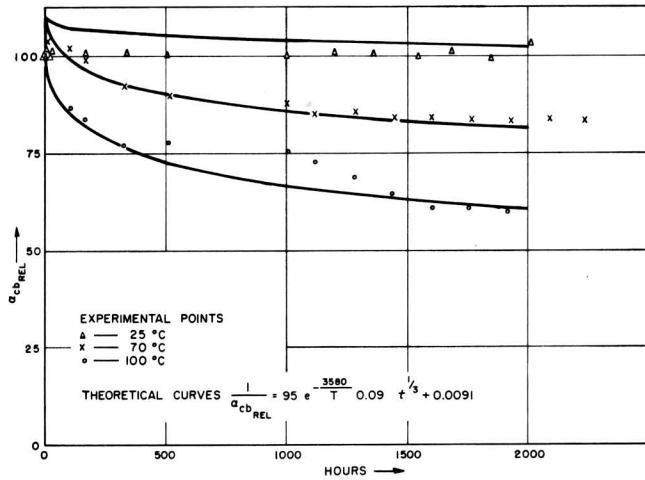


Fig. 6 - Life test results for vacuum sealed (10^{-4} mm Hg) transistors. (R. R. Johnson)

To test the theory describing these results, especially the temperature dependence of the oxide growth, a room temperature life test was run, the results of which are shown in Fig. 7. These transistors were sealed in hermetic cans in dry air without silicone. The results are also shown in Fig. 9, where each point is an average of five transistors and again the spread is shown. In analyzing this test, the three transistors with low α_{cb} have been discarded.

Outline of Method of Analysis

The thickness of the growing GeO_2 layer cannot be very large at the temperature and times dealt with in this report, 25 degrees C to 125 degrees C. As will be shown

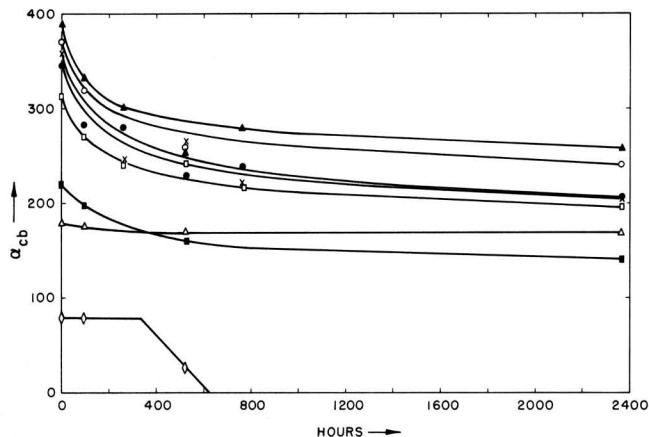


Fig. 7 - Life test results for transistors sealed in dry air. Shelf life at room temperature. (E. L. Jordan)

later this growth certainly cannot exceed a hundred monolayers. It is reasonable therefore to assume that the increase of the surface recombination velocity s , is directly proportional to the increase of the thickness of the layer. For $\Delta w \ll w$

$$\frac{ds}{dt} = p \times \frac{dw}{dt}, \quad (4)$$

where w is the thickness of the GeO_2 layer and p is a proportionality factor. Upon integration,

$$s = s_0 + p \times w \quad (5)$$

As is well known, α_{cb} is directly related to the surface recombination velocity through Eq. 6.13

$$\frac{1}{\alpha_{cb}} = C_5 \times s + C_6 \quad (6)$$

where C_5 and C_6 are given by geometry, material, etc. of the transistor.

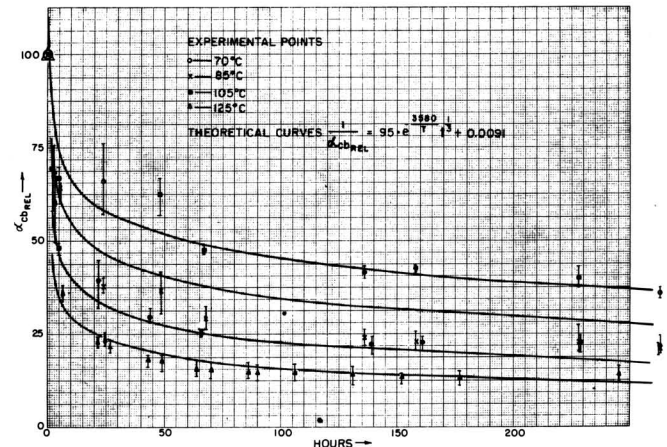


Fig. 8 - Fig. 2-5 replotted using average of relative values of α_{cb} . Range within which values fall is indicated.

Combination of Eqs. 5 and 6 then gives

$$\frac{1}{\alpha_{cb}} = \frac{1}{\alpha_{cb_0}} + C_5 p w \quad (7)$$

where

$$\frac{1}{\alpha_{cb_0}} = C_5 \times s_0 + C_6$$

Now by insertion of experimental results of a_{cb} versus time in Eq. 7, the growth rate of the oxide layer can be obtained from the resulting relation of w versus time.

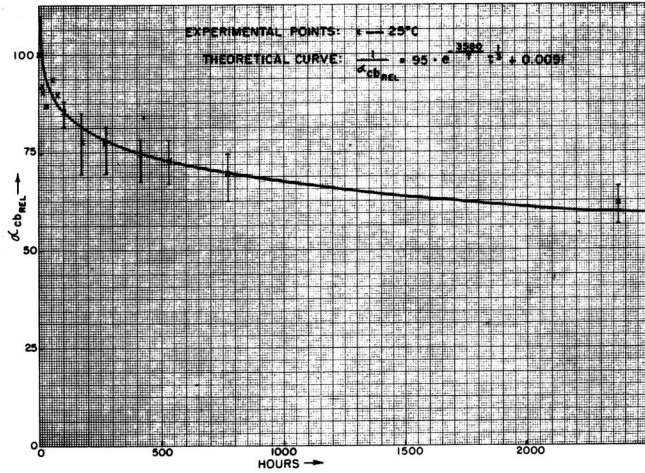


Fig. 9 – Fig. 7 replotted using average of relative values of a_{cb} . Range within which values fall is indicated.

Analysis of the Data

It is well known that within a certain temperature range the oxidation process follows one of a small number of possible rate equations.^{14, 15} Using Eq. 7, it is now possible to fit the rate equations to the experimental data. It is then found that the so-called "cubic" rate equation,

$$d = C_7 \times t^n + C_8, \quad (8)$$

where $n = 1/3$

fits the data very well while none of the other rate equations can account for the initial drop. In Figs. 10 and 11 experimental points from Fig. 8 have been redrawn and a number of possible rate equations have been fitted at two points. As can be seen good fit can only be claimed for the "cubic."

Equation 8 applies to the case of oxidation of a metal with a thin oxide layer. The condition of a thin oxide layer (<500 Å) is certainly valid as shown in the direct oxidation experiment.

In Eq. 8, the coefficient C_7 contains an exponential factor characterizing the activation energy for oxidation. Thus Eq. 6 can be written as

$$\frac{1}{a_{cb}} = C_9 e^{-\frac{C_{10}}{T}} t^{1/3} + C_6 \quad (9)$$

Equation 9 has been fitted to the experimental points in Fig. 8 using coincidence at two arbitrary points, namely 20 hours and 160 hours. The result is the following equation

$$\frac{1}{a_{cb}} = 95 e^{-\frac{3600}{T}} t^{1/3} + 0.0091 \quad (10)$$

which has been used to draw the curves in Fig. 8. As can be seen in Fig. 9, this equation fits the room temperature curve also.

We can press the fit a little further. At a first glance, it is surprising that the theoretical curves according to Eq. 10, do not go through the point 0,100, in other words, that the constant in Eq. 10 is not 0.01. However, it has been found that when transistors are taken off a high temperature life test, say 85 degrees C, and brought to room temperature for the purpose of measurements, a_{cb} shows a decline for about 48 hours¹⁶ as shown in Fig. 12. This fact was not known at the time of the life test

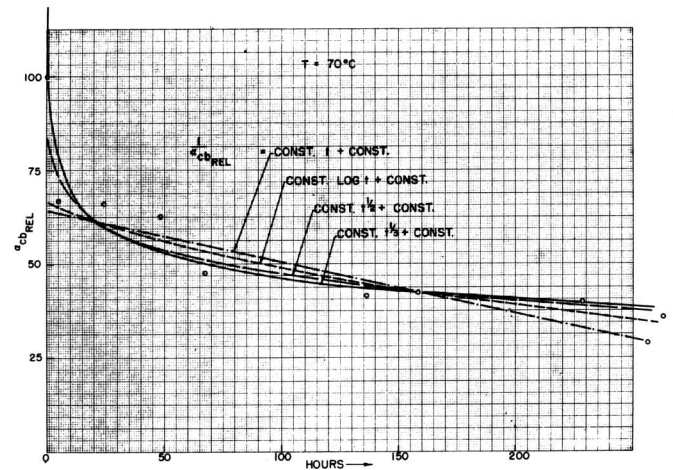


Fig. 10 – Some known oxidation equations fitted to the 70°C curve of Fig. 8.

described above and therefore no time interval was fixed between removal from life test and measurement. The procedure was to remove the units in the morning and to measure them at any time during that day. It may therefore be assumed that an average of four hours elapsed between removal and measurement, corresponding to a decline in a_{cb} of about 9 percent as shown in Fig. 12 (This fact at the same time may explain some of the spread of the measured a_{cb} values.) However, the initial a_{cb} was measured before any heat treatment and therefore would correspond to the end value in Fig. 12. It may be expected then that all the points except the initial reading are about 9 percent too high as indeed seems to be borne out by Eq. 10. When the measurements are corrected for this effect they obey Eq. 11

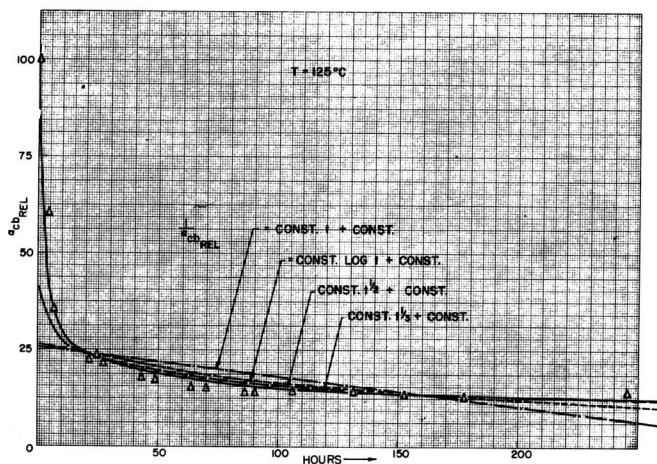


Fig. 11 – Some known oxidation equations fitted to the 105°C curve of Fig. 8.

$$\frac{1}{\alpha_{cb}} = 95 e^{-\frac{3600}{T}} t^{1/3} + 0.01 \quad (11)$$

The value of the activation energy in Eq. 10, 7200 cal/mol at first seems unusually small. Recent work on the oxidation of copper,¹⁷ which according to the reasoning outlined above follows a similar oxidation process, and suggests a small activation energy, about 9000 cal/mol.

Direct Oxidation Experiment

To verify the oxidation hypothesis which is used to explain slow decay of α_{cb} of p-n-p transistors, the following experiment was performed. Samples of n-type germanium were heated in an oven at 85 degrees C for selected periods of time. Subsequently the samples were washed in a sodium hydroxide solution to remove any oxide formed. The solution was then analyzed quantitatively by a spectrographic method for the amount of germanium present. These results are shown in Fig. 13. The experimental points are in reasonable agreement with the cubic-root-of-time law suggested earlier. To retain the oxide in easily soluble form it was found necessary to keep the samples at 100 percent relative humidity during the heat treatment.

The results shown in Fig. 13 makes it possible to deduce a quantitative expression for the oxidation rate. Assuming that at the low relative humidity present in encapsulated transistors the oxidation rate is not higher but may be lower than the rate at 100 percent relative humidity. Then the following expression gives an upper limit for the oxide layer thickness in Å at 85 degrees C.

$$w \leq 21 (t + 1.3)^{1/3} \quad (12)$$

It should be pointed out that this oxidation rate is valid for an etched, and consequently hydrated, surface and therefore may be higher than for a clean germanium surface.

Influence of a Sequence of Temperatures

From the picture outlined above some predictions may be made about the influence of oxidation on units that are subjected to a sequence of temperatures. As an example, consider transistors that are first aged in air at room temperature for 24 hours. Following this they are heated for 24 hours at 105 degrees C. With the help of Eq. 10 we may now follow the change in α_{cb} due to oxidation. After the first 24 hour-room temperature aging, the relative α_{cb} is down from 100 percent to 85 percent. After the next 24 hour-105 degrees aging period, the relative α_{cb} is down further to 30 percent of the initial value.

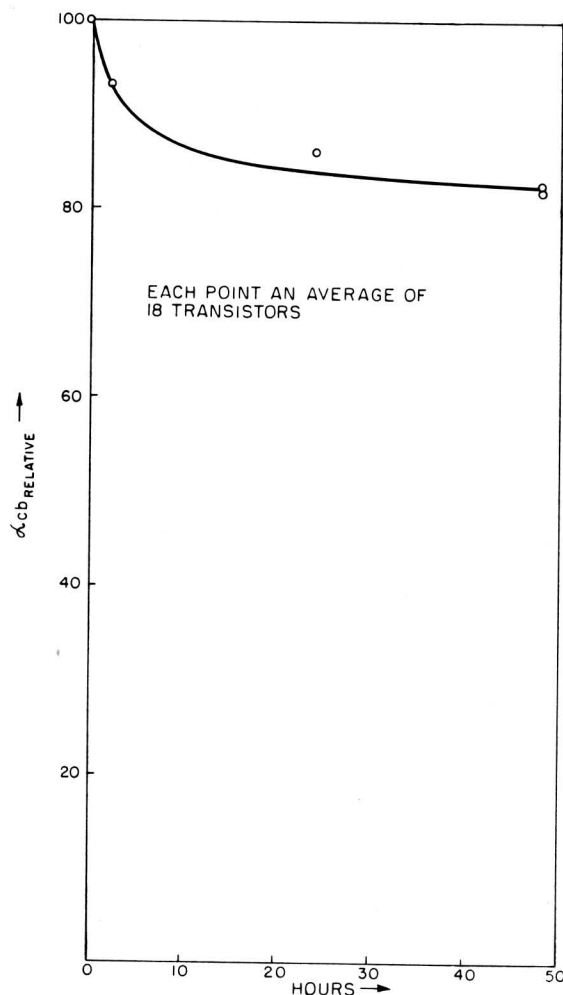


Fig. 12 – Off-life decline of α_{cb} ("48 - hour effect"). (R. R. Johnson)

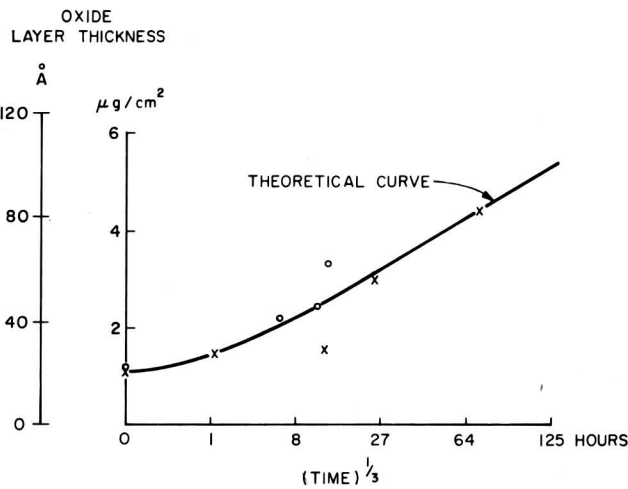


Fig. 13 - Thickness of oxide layer versus time.

From then on at a temperature of 85 degrees C, the related a_{cb} can be predicted from the following time dependent expression

$$\frac{1}{a_{cb_{rel}}} = 0.00427 (t + 160)^{1/3} + 0.033. \quad (13)$$

Alternatively, assuming that the value of a_{cb} at the start of the 85 degrees C shelf life test is 100 percent, and that all measurements (except the initial one) are made an average of 4 hours after removal from the oven, we have

$$\frac{1}{a_{cb_{rel}}} = \frac{1}{3.3 \times 1.09} [0.00427 (t + 160)^{1/3} + 0.033] \quad (14)$$

This relation is plotted in Fig. 14. In a similar manner the results of any combination of temperature and aging time can be predicted. In Fig. 14 are also shown some experimental points from life tests of units that have been subjected to the previously mentioned sequence of temperatures.

The first constant in Eq. 12 will be different for different types of transistors and depends on the ratio of C_5/C_6 in Eq. 6.

It should be pointed out again that factors other than oxidation may influence a_{cb} during life. However, interpretation of other effects is difficult unless the influence of oxidation is first separated.

Conclusions

From the evidence presented, it appears that in germanium p-n-p transistors which have been electrolytically etched in potassium hydroxide and subsequently

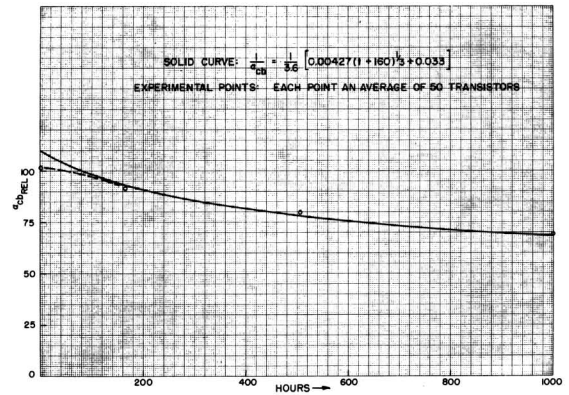


Fig. 14 - Theoretical curve and experimental value of a_{cb} for shelf life at 85°C. (A. Kerken, S. C. Simons)

hermetically sealed, a_{cb} is influenced by oxidation in the following way:

1. The conventional electrolytic etch in 40 percent potassium hydroxide leaves a composite hydrated oxide layer, $\text{GeO} - \text{GeO}_2$, on the surface.
2. The high a_{cb} resulting from this etch is mainly a consequence of the GeO layer.
3. The GeO_2 layer will grow with time and the decay of a_{cb} is a consequence of this growth.
4. The value of a_{cb} after storage of a p-n-p germanium transistor at a temperature T degrees K can be predicted from

$$\frac{a_{cb_0}}{a_{cb}} - 1 = C_1 e^{-\frac{3600}{T}} (t + t_0)^{1/3}$$

where a_{cb_0} is the initial value after electrolytic etching.

C_1 is a constant which depends on the geometry of the transistor. For a 2 N 77 transistor, $C_1 = 95$.

t_0 refers to the oxide thickness at the start of the storage period and is the time necessary to grow this thickness at the temperature T . t_0 may be obtained from

$$\frac{a_{cb_0}}{a_{cb_1}} - 1 = C_1 e^{-\frac{3600}{T}} t_0^{1/3}$$

where a_{cb_1} is the value at the start of the storage period.

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