

Some Failure Modes of Double Diffused Silicon Mesa Transistors

A. A. BERGH
Bell Telephone Laboratories, Inc.
Allentown, Pennsylvania

ABSTRACT

THIS paper discusses two different failure modes (bulk failure and surface failure) which have been observed on double diffused silicon n-p-n mesa transistors. (a) In the presence of bare copper in an oxygen free ambient, power aging degrades the emitter parameters and gain. Only partial recovery can be achieved by etching into the bulk silicon or by heating the device at 300°C (bulk failure). (b) In gold plated and/or oxygen backfilled cans, soft, loopy reverse junction characteristics develop under both temperature and power agings, first on the collector and later on the emitter. Both junctions recover completely upon opening the can and drying the transistor surface (surface failure).

Surface failure is caused by water adsorption over the surface of the silicon wafer. Experimental evidence, including aging experiments in atomic hydrogen, is presented to demonstrate that the bulk failure is caused by copper contamination in the bulk silicon. Copper is transferred from the can to the wafer via a volatile hydride. It diffuses into the silicon and becomes electrically active during power aging.

Qualitative explanations are offered for both failure modes. Surface failure is due to surface states introduced by the adsorbed water and/or ionic conduction. In order to explain bulk failure, the solubility and precipitation of copper is examined over the transistor profile and the effect of field on the migration of copper in silicon is taken into account.

INTRODUCTION

The purpose of this paper is to explore different failure modes and mechanisms of a medium power double diffused n-p-n silicon mesa transistor. The effect of the enclosure on the reliability of the device has been observed before⁽¹⁾; the important findings can be given as follows:

1. Transistors enclosed in evacuated or nitrogen backfilled copper cans and

operated at current densities of 200-400 mA per mm of emitter perimeter show a rapid deterioration in BV_{EBO} and h_{FE} .

2. The above failure can be prevented by either (a) keeping the junction temperature below 55°C with a heat sink, or by (b) backfilling the device enclosure with oxygen.
3. The occurrence of BV_{EBO} and h_{FE} deterioration during power aging is considerably delayed by using gold plated copper cans.
4. Oxygen in the gold plated cans completely eliminates the emitter degradation but it gives rise to a collector failure. This occurs on both temperature and power agings as opposed to the emitter degradation which is observed only after high current operation.

The reproducibility of the above effects and the relatively short aging times required (< 16 hrs.) rendered this device an ideal vehicle to study the cause and mechanism of the different failure modes. A large number of devices were aged under different conditions and an attempt was made to recover the degraded units. It was found that the emitter failure is caused by a change in the bulk material while the collector degradation is due to a surface effect. A qualitative summary of the failure modes and recoveries is given in Table I. A quantitative account follows the description of the device and the aging experiments.

TABLE I
FAILURE MODES

<i>Conditions to Cause Failure</i>	<i>Parameters Affected</i>	<i>Modes of Recovery</i>										
1. Bulk Effect												
Simultaneous presence of												
<table style="border: none;"> <tr><td>Bare copper</td><td rowspan="4" style="font-size: 3em; vertical-align: middle;">}</td></tr> <tr><td>No oxygen</td></tr> <tr><td>High current</td></tr> <tr><td>High temperature</td></tr> </table>	Bare copper	}	No oxygen	High current	High temperature	<table style="border: none;"> <tr><td>I_{EBO}</td><td rowspan="4" style="font-size: 3em; vertical-align: middle;">}</td></tr> <tr><td>BV_{EBO}</td></tr> <tr><td>h_{FE}</td></tr> <tr><td>I_{CBO}</td></tr> </table>	I_{EBO}	}	BV_{EBO}	h_{FE}	I_{CBO}	Partial recovery by etching into Si wafer, or prolonged heating at 300°C .
Bare copper	}											
No oxygen												
High current												
High temperature												
I_{EBO}	}											
BV_{EBO}												
h_{FE}												
I_{CBO}												
2. Surface Effect												
<table style="border: none;"> <tr><td>Oxygen ambient</td><td rowspan="2" style="font-size: 3em; vertical-align: middle;">}</td></tr> <tr><td>High temperature</td></tr> </table>	Oxygen ambient	}	High temperature	<table style="border: none;"> <tr><td>First: I_{CBO}</td><td rowspan="2" style="font-size: 3em; vertical-align: middle;">}</td></tr> <tr><td>BV_{CBO}</td></tr> <tr><td>Later: I_{EBO}</td><td rowspan="2" style="font-size: 3em; vertical-align: middle;">}</td></tr> <tr><td>BV_{EBO}</td></tr> </table>	First: I_{CBO}	}	BV_{CBO}	Later: I_{EBO}	}	BV_{EBO}	Complete recovery by drying the surface of the wafer, recovery is instantaneous.	
Oxygen ambient	}											
High temperature												
First: I_{CBO}	}											
BV_{CBO}												
Later: I_{EBO}	}											
BV_{EBO}												

EXPERIMENTAL

Figure 1 shows the top view and the cross section of the silicon wafer. A schematic diagram of the header assembly is given in Figure 2. The header was

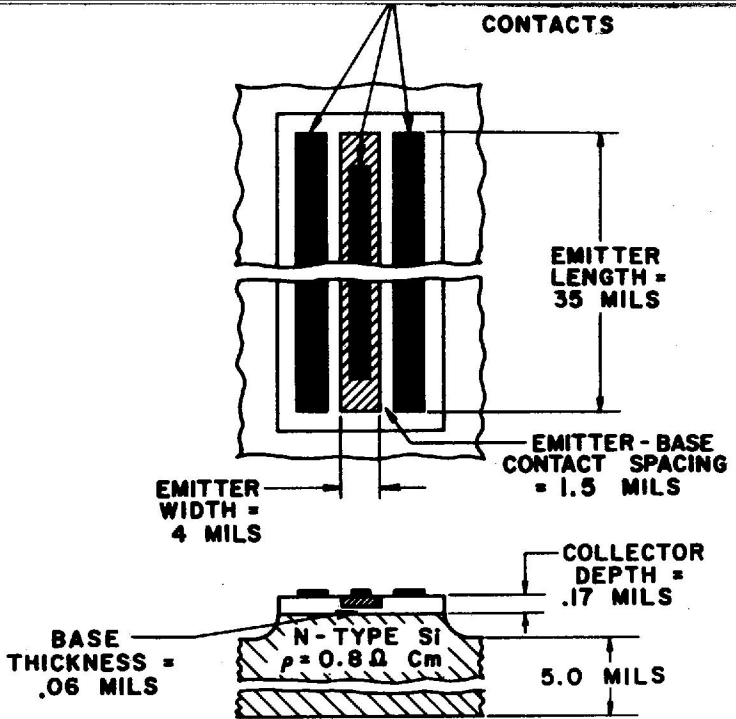


FIG. 1. Medium Power n-p-n Silicon Mesa Transistor

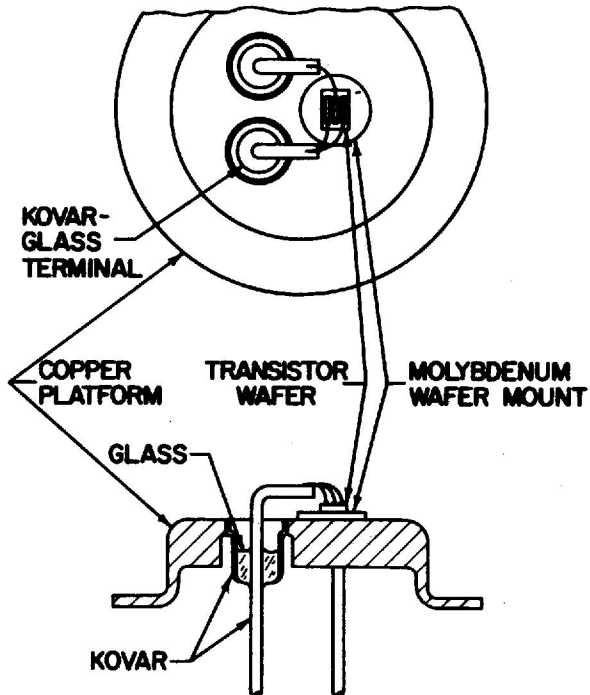


FIG. 2. Schematic Diagram of the Header Assembly

gold plated before mounting the silicon wafer. A tubulated copper can precleaned in hydrogen at 450°C was cold-welded to the header assembly. The important steps in the encapsulation process are listed below:

1. Following a light etch in dilute HF the header assembly was heated in wet oxygen at 250°C for 16 hrs.
2. After welding the can to the header the device enclosure was evacuated to lower than 10^{-4} torr of pressure at 300°C for 40 minutes and sealed or backfilled with different gases.
3. The encapsulated devices were heated for several hours at 250°C, and tested for leakage and mechanical strength.

Temperature aging was carried out at 300°C in room air. The collector current was 400 mA (12 watts) during power aging. The average junction temperature was approximately 200°C. Deterioration of BV_{EBO} usually began after the first hour of aging and a decrease by more than 50% of the original value has been observed on all devices encapsulated in oxygen-free copper cans after aging for 16 hrs. The collector usually started to degrade in oxygen backfilled cans after continuous temperature or power aging in excess of one week. A detailed account of the aging results is given below.

AGING RESULTS

Typical reverse characteristics of the transistor junctions for bulk and surface failures and recovered devices are shown in Figure 3.

Bulk Failures

Table 2 gives the changes in the electrical characteristics after power aging for 16 hrs. in evacuated copper cans. Deterioration of the emitter characteristics is accompanied by a relatively small change in I_{CBO} .

TABLE 2
DEGRADATION DUE TO BULK EFFECTS

Evacuated Cu Can, Power Aged for 16 Hours

(Average of 16 Transistors)

Parameter	Unit	Before Aging	After Aging	Test Conditions
I_{EBO}	μA	0.06	78.0	$V_{EB} = 2V$
BV_{EBO}	V	9.7	3.0	$I_E = 100 \mu A$
h_{FE}		22	6.1	$I_C = 1 mA, V_{CE} = 5V$
I_{CBO}	μA	0.13	6.3	$V_{EB} = 20V$

Insignificant change in: BV_{CBO} , BV_{CES} ,
 $V_{CE\ sat}$, f_t

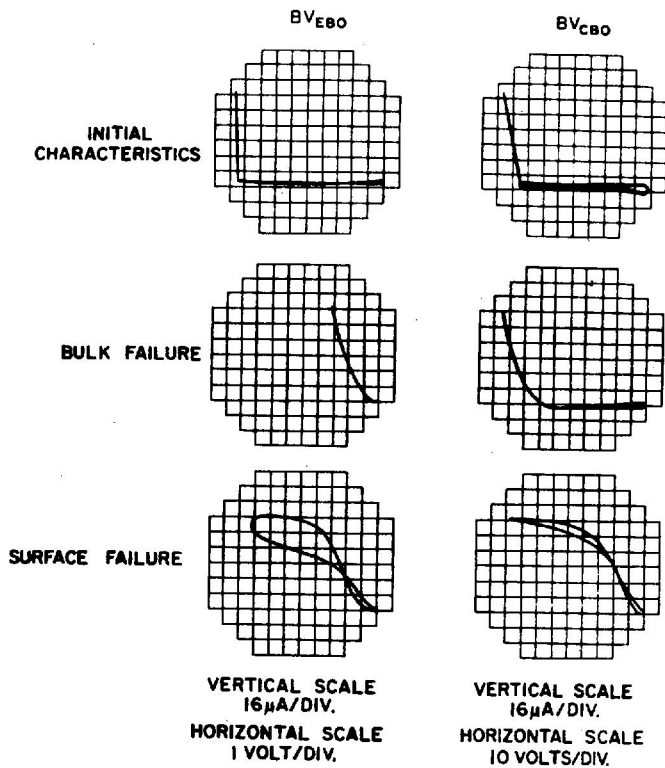


FIG. 3. Typical Reverse Characteristics

After aging and testing, the cans were removed and an attempt was made to recover the device by etching. The header was coated with Apiezon-W wax to avoid contamination during etching. The composition of the etchant was 50:50:1 HNO_3 (60%) : water: HF (49%). A rinse in a 10% solution of KCN and DI water preceded and followed each etching. The time necessary to recover bulk failures is increased for decreasing BV_{EBO} values as shown in Figure 4. While BV_{EBO} increased leakage currents could be only partially recovered as shown in Table 3.

TABLE 3
RECOVERY OF BULK DEGRADATION BY ETCHING*

Average of 6 Transistors

Parameter	Unit	Before Power Aging	After Power Aging	After Etch
I_{EBO}	μA	0.26	12.5	2.37
BV_{EBO}	V	9.7	3.5	7.9
I_{CBO}	μA	0.16	1.2	1.14

*Etchant 50:50:1 HNO_3 (60%) : Water: HF (49%)

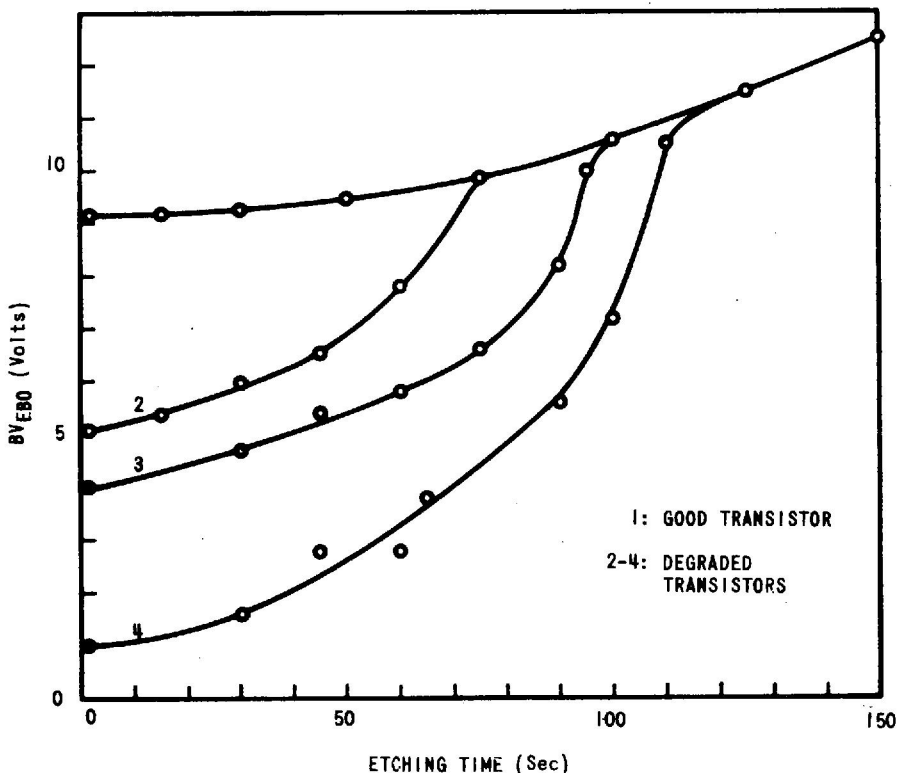


FIG. 4. Recovery of BV_{EBO} During Etching

Similar recovery was obtained by heating the degraded units in closed cans at 300°C for over 70 hours. Although BV_{EBO} increased to values higher than 7 volts within the first 18 hours, I_{EBO} was typically an order of magnitude higher than the initial value even after 72 hours.

Surface Failure

Typical values of surface degradation and recovery are shown in Table 4. Changes are most pronounced at the collector junction. Instantaneous recovery is obtained by opening the can and blowing dry gas over the transistor wafer. The loopy reverse characteristics shown in Figure 3 could be re-established by testing the device in a high relative humidity ambient and complete recovery was observed after lowering the humidity level of the ambient. The above results indicate that surface failure is caused by water. Since water was found only in the oxygen backfilled can, there must be some hydrogen in the device ambient. The transformation of hydrogen into water thus eliminated the bulk failure and introduced the surface degradation. The source of hydrogen in the enclosure is probably the copper can and the gold plating on the header and can. In order

TABLE 4
 SURFACE DEGRADATION AND RECOVERY
 (Gold Plated Copper Can Backfilled with Oxygen. Power Aged for 200 Hours)

<i>Parameter</i>	<i>Unit</i>	<i>After Degradation</i>	<i>After Recovery</i>	<i>Initial</i>
I _{CBO}	Amp.	3×10^{-5}	5×10^{-8}	5×10^{-8}
BV _{CBO}	Volts	68	90	90
I _{EBO}	Amp.	3.2×10^{-8}	2×10^{-9}	2×10^{-9}
BV _{EBO}	Volts	7.6	10	10

to establish the role of hydrogen in the bulk degradation, experiments were carried out in the most active form of hydrogen, i.e., atomic hydrogen.

AGING EXPERIMENTS IN ATOMIC HYDROGEN

Atomic hydrogen was generated in the ac field of a 10-16 mc radio frequency generator. A schematic diagram of the electrodeless discharge apparatus is shown in Figure 5, and the system is described in detail elsewhere.⁽²⁾ A continuous flow of hydrogen was maintained by a mechanical pump and a variable leak, keeping the pressure close to 0.2 torr. The transistor was placed into a side arm and it was connected to the power supply and/or the test set with flexible lead wires. Since the atomic hydrogen was generated in the area confined by the electrostatic screen, it could reach the transistor only by diffusion. The concentration of atomic hydrogen at the device was therefore determined by its position in the side arm which could be adjusted with a removable outside magnet. The concentration of the atomic hydrogen is important to control the temperature of the device. Recombination at the contacts, lead wires and other high recombination generates excess heat and destroys the device. The atomic hydrogen concentration was adjusted so that the junction temperature should not exceed 300°C during the simultaneous application of atomic hydrogen and power aging.

Summary of the aging experiments is presented in Table 5. Treatment "H₂" indicates that the R.F. generator was turned off. A large deterioration in the emitter characteristics was observed upon exposure to atomic hydrogen and power if a bare copper surface was exposed between the atomic source and the device. High purity, spectroscopic grade copper was used to establish that Cu and not an impurity in the copper can is responsible for the degradation. After prolonged exposure of copper surfaces a light copper mirror was deposited on the walls of the side arm next to the transistor. Exposure to atomic hydrogen in the absence of bare copper had no effect on the device characteristics.

In order to determine the effect of high current density on the deterioration of the device, exposure to atomic hydrogen was alternated with power aging for

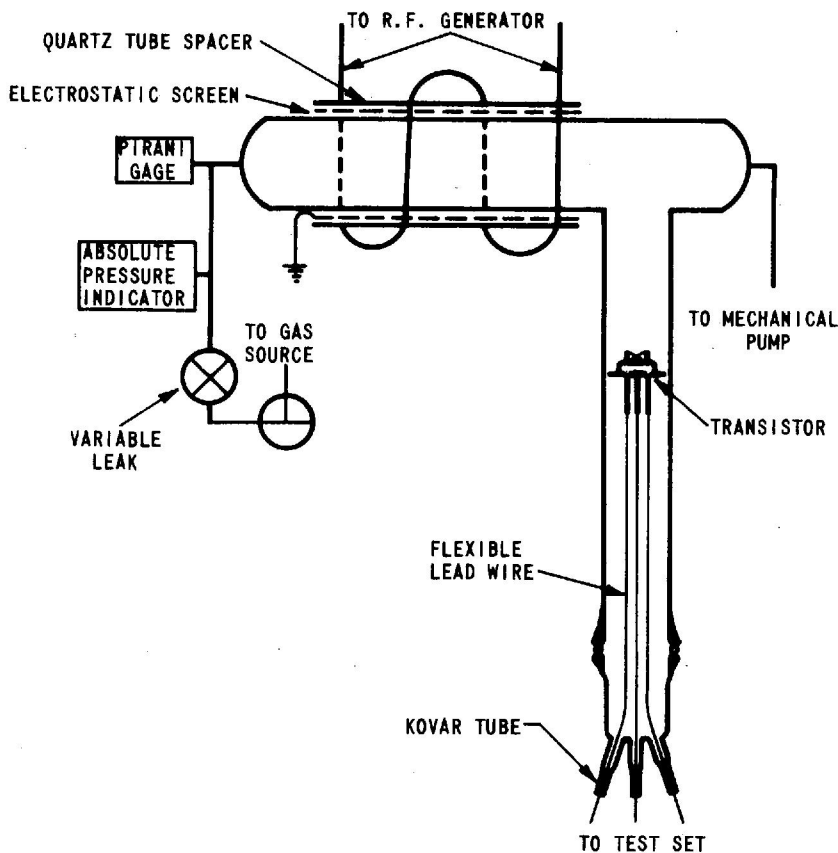


FIG. 5. Schematic Diagram of the Electrodeless Discharge Apparatus

TABLE 5
SUMMARY OF AGING EXPERIMENTS IN HYDROGEN
(2 Hours Experiments, $\tau_1 = 150\text{-}300^\circ\text{C}$)

Encapsulation	Treatment	ΔBV_{EBO} , Volts
No can	H ₂ + P	0
No can	H + P	0
Opened Cu can	H ₂ + P	0
Opened Cu can	H ₂ + P (150°C)*	2-3
Opened Cu can	H + P	6-8
No can		
Spectroscopic grade		
Cu adjacent to header	H + P	6-8

H₂ = molecular hydrogen 0.1 - 0.3 torr
H = atomic hydrogen 0.1 - 0.3 torr
P = power aging, 2 watts

*Side arm kept at 150°C with an outside heat source

30 minute intervals for a device with opened copper can. The results are shown in Figure 6. Exposure to atomic hydrogen had almost no effect on BV_{EBO} . A large decrease resulted, however, during the subsequent power aging. On the other hand, power aging had no effect unless preceded by exposure to atomic hydrogen in the presence of copper:

The results of the atomic hydrogen experiments can be summarized as follows: (1) Emitter degradation occurs only during power aging if the application of high current density is accompanied or preceded by the exposure to atomic hydrogen in the presence of copper; (2) The degradation is identical to that experienced in bare copper cans with oxygen free ambient. This implies that: (1) Atomic hydrogen transfers copper from the exposed metal surface to the transistor wafer; and (2) The copper over the silicon wafer degrades the emitter junction during power aging. (3) The similar results with can material (OFHC grade Cu) and spectroscopic grade copper indicate that Cu and not another impurity in the can is causing the emitter degradation.

Experiments to substantiate the above conclusions are described below.

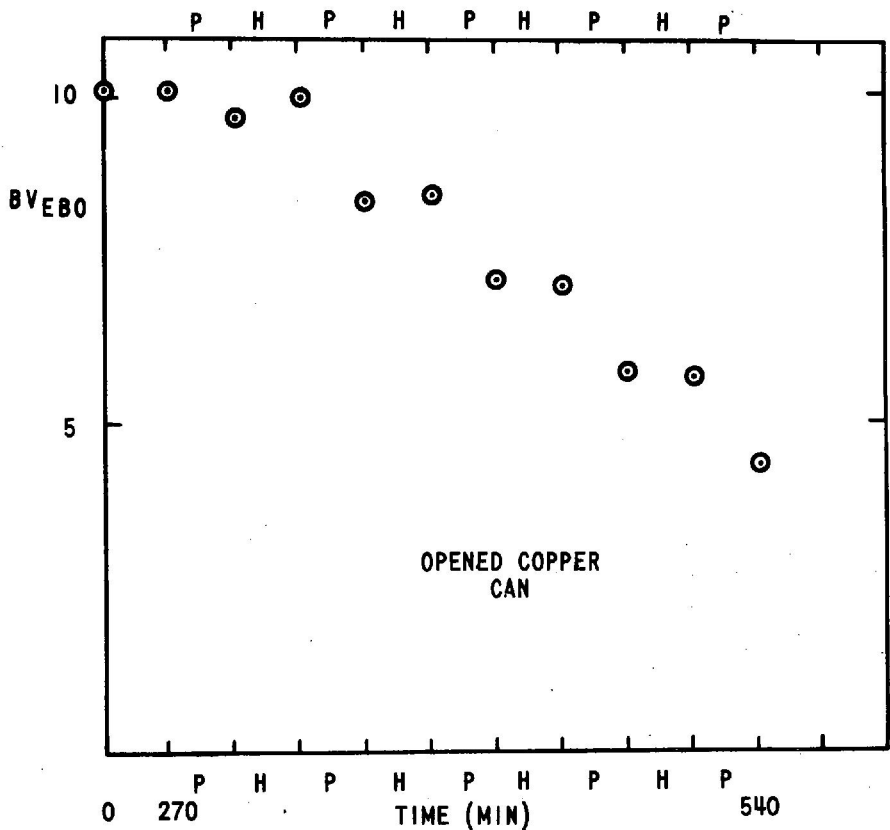


FIG. 6. Change in BV_{EBO} During Alternating Aging for 30 Min. Periods in Atomic Hydrogen (H) and Power (P). (20C Type Medium Power Silicon n-p-n Mesa Transistors)

Freshly reduced copper forms a volatile hydride upon exposure to molecular hydrogen at 250° to 400°C. This hydride is unstable, it decomposes on the walls of the apparatus forming a copper mirror.⁽³⁾ The formation of a transient hydride has been also reported by the action of atomic hydrogen on copper.⁽⁴⁾ This material is unstable in air, forming a copper oxide rapidly. The transport of copper in atomic hydrogen was apparent in our experiments by the mirror formed on the walls adjacent to the transistor.

Metal precipitates have been noted to cause rounded reverse characteristics on diodes due to excess current below the avalanche breakdown voltage.⁽⁵⁻⁷⁾ We have deposited small amounts of copper by replacement plating over the transistor wafers and encapsulated the devices into evacuated, gold plated cans. The emitter degradation during power aging was similar to that observed for transistors in bare copper cans.

Thus, both the transfer of copper by hydrogen and the deterioration of the device due to copper could be considered to explain the bulk failure. In order to assure that metallic copper and not another contamination in the enclosure contributes to the degradation a series of experiments was carried out using gold plated copper cans. Copper pieces approximately 6 mm in diameter were placed into gold plated, evacuated enclosures and the transistors were power aged for 16 hrs. The results are summarized in Table 6.

TABLE 6

*THE EFFECT OF METALS IN THE DEVICE ENCLOSURE
EVACUATED* GOLD PLATED COPPER CAN, POWER AGED FOR 16 HOURS*

<i>Metal</i>	ΔBV_{EBO} , <i>Volts</i>
None	0
Spectroscopic Grade Cu	5-8
OFHC Cu	6-8
OFHC Cu Oxidized in "Ebanol C"	0

* $\Delta BV_{EBO} = 0$ in all cans backfilled with O₂.

All transistors degraded with bare copper in the enclosure independent of the purity level of the metal. No change was observed after power aging in cans oxidized with "Ebanol C special"* or backfilled with oxygen. It can be concluded, therefore, that copper and not its impurities are responsible for the bulk degradation, and a transfer mechanism similar to that observed in atomic hydrogen is causing the bulk degradation. Direct evidence for the copper transfer in the device enclosure was obtained by placing 6 mm diameter clean silicon wafers into bare copper enclosures which were evacuated or backfilled with

*Product of Ethone Inc., New Haven, Conn.

forming gas (10% H₂, 90% N₂). After heating the cans for 16 hrs. at 300°C solid source mass spectrograph analysis detected copper on both types of wafers but the concentration was higher by a factor of 8 on those enclosed in forming gas.

DISCUSSION

The cause of the failure modes has been established. Qualitative models of the mechanisms are suggested below:

Surface Failure

Water can introduce shallow donor type surface states on nonoxidized silicon surfaces⁽⁸⁾ or it can ionize surface impurities and give rise to channels by ionic conduction.⁽⁹⁾ Since repeated cleaning of the device in organic solvents, 10% solutions of KCN and high purity water did not alter the effect of the water vapor, ionic conduction was probably unimportant in our experiments.

Bulk Failure

In order to postulate a mechanism for the bulk degradation the following experimental facts must be explained. (1) Copper affects predominantly the emitter junction characteristics. (2) High current and high temperature must be simultaneously present to cause degradation. (3) The etching time to recover the emitter is proportional to the decrease in BV_{EBO} during aging. (4) Temperature aging alone, at 300°C, does not affect the transistor and, in fact, partially recovers a device degraded by power aging.

An excellent and comprehensive study of the diffusion and solubility of copper in silicon was published by Hall and Racette.⁽¹⁰⁾ They showed that interstitial copper is a single donor and substitutional copper is a triple acceptor in silicon. The solubility is therefore directly proportional to the hole concentration in p-type material and increases with the cube of the free electron concentration in n-type material. Since the doping level is the highest in the emitter for both n-p-n and p-n-p double diffused transistors the copper concentration is highest in the emitter. This might be further increased by the large number of crystal imperfections introduced during the emitter diffusion.⁽¹¹⁾

The precipitation of copper in silicon has been noted before,^(5, 10) the rate of precipitation being higher with increasing supersaturation. Local hot spots during high current operation can give rise to supersaturation unless the over-all junction temperature is kept low by a heat sink. The supersaturated copper precipitates during cooling and it redistributes over the entire emitter region during temperature aging. Another way to remove the precipitated copper is chemical etching. The fact that the etching time to recover the emitter is proportional to the amount of degradation indicates that copper diffuses into the silicon during aging. Precipitates form, therefore, at deeper regions of the emitter space charge region as aging progresses.

REFERENCES

1. N. J. CHAPLIN, D. M. HILL, private communication.
2. A. A. BERGH, paper to be published in the *Bell System Technical Journal*, February, 1965.
3. D. T. HURD, *An Introduction to the Chemistry of Hydrides*, p. 194, John Wiley, N.Y. (1952).
4. PIETSCH and JOSEPHY, *Naturwiss.*, 19, 737 (1931).
5. A. GOETZBERGER and W. SHOCKLEY, *J. Appl. Phys.* 31, 1831 (1960).
6. S. M. HENNING and L. E. MILLER, "Emitter Softening in Diffused Silicon Transistors," *Proc. Phys. of Failure Symposium*, p. 43 (1965).
7. J. E. LAWRENCE, "Electrically Active Metallic Impurity Segregates in Silicon Crystals." Paper presented at Fall Meeting of Electrochemical Society, October 11-15, 1964, Washington, D.C.
8. T. M. BUCK and F. S. MCKIM, "Effect of Certain Chemical Treatments and Ambient Atmospheres on Surface Properties of Silicon," *J. Electrochem. Soc.* 105, 709 (1958).
LITVINON, R. and HSU, T., in "Surface Properties of Semiconductors" edited by A. N. FRUMKIN, Consultants Bureau, 1964, p. 165.
9. M. M. ATALLA, A. R. BRAY and R. LINDNER, "Stability of Thermally Oxidized Silicon Junctions in Wet Atmospheres," *Suppl. Proc. Inst. Elec. Engrs.* (London) p. 4, B106, 1130 (1959).
W. SHOCKLEY, H. J. QUEISSER and W. W. HOOPER, "Charges on Oxidized Silicon Surfaces," *Phys. Rev. Letts.*, 11, 489 (1963).
W. SHOCKLEY, W. HOOPER, H. J. QUEISSER and W. SCHROEN, "Mobile Electric Charges on Oxide-Covered Silicon p-n Junctions," International Conference on the Physics and Chemistry of Solid Surfaces, Brown University, June 1964, paper VV.
10. R. N. HALL and J. H. RACETTE, *J. Appl. Phys.*, 35, 379 (1964).
11. R. J. Jaccodine, *Appl. Phys. Letters*, 4, 114 (1964).