Feb. 24, 1959 W. F. HALDEMAN 2,874,448

METHOD FOR STABILIZING SEMI-CONDUCTOR RECTIFIERS

Filed Feb. 13, 1953

FIG 1

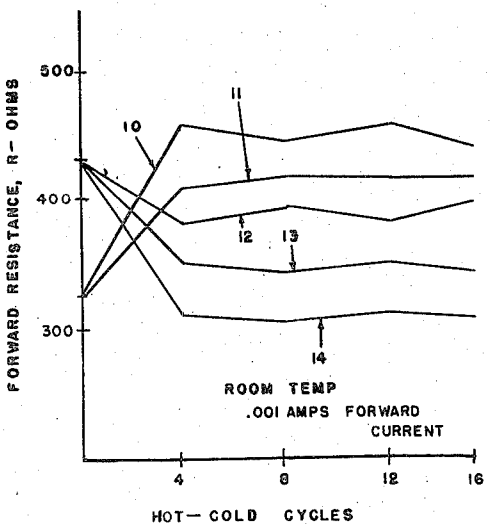


FIG 2

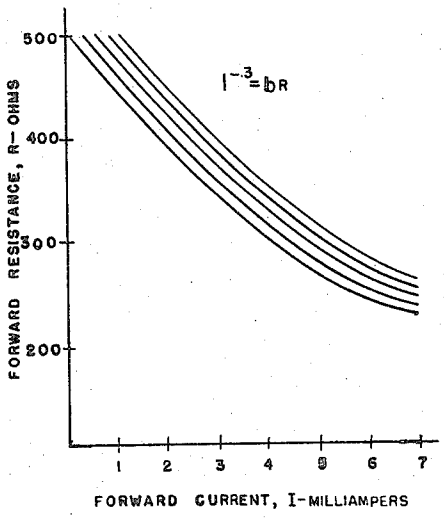
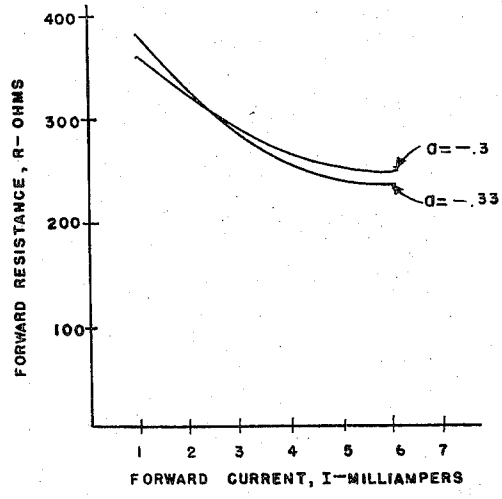


FIG 3



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2,874,448

METHOD FOR STABILIZING SEMI-CONDUCTOR RECTIFIERS

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9 Claims. (Cl. 29—25.3)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

My invention relates to semiconductor-type rectifiers and is particularly directed to methods and means for stabilizing the resistance-current characteristics of said rectifiers.

It has long been known that two dissimilar metals placed in contact have unidirectional current carrying characteristics and in recent years the metal germanium has been extensively used as one of these metals, the second metal being a cat whisker made of steel or a non-ferrous metal spring-pressed into contact with the germanium. In an effort to accentuate the unidirectionality of such a rectifier and to standardize the current-resistance characteristics, the germanium is melted with a fraction of a percentage of an impurity and permitted to cool slowly. In spite of care in preparing the germanium ingot there is found to be radical variations in electrical characteristics among different ingots and among different parts of each ingot. Worse, the germanium changes its characteristics with aging, thus upsetting circuitry in which it has been incorporated and calibrated.

I have found that commercial semiconductor-type rectifiers have resistance-current characteristics that may be defined by the expression

$$I^{-a}=bR$$

where I is current of the order of a few milliamperes, R is an effective resistance in ohms, hereinafter defined, and a and b are constants. The exponent a determines the curvature of the exponential resistance curve of any one semiconductor rectifier at one temperature. It is variations of these constants, a and b, after manufacture that is particularly troublesome. In my co-pending application entitled "Testing Semi-Conductor Rectifiers," Serial No. 336,893, filed February 13, 1953, issued on April 24, 1956, as U. S. Patent No. 2,743,420, I describe in detail how rectifiers may be tested and grouped according to their constants a and b.

The object of this invention is an improved method of stabilizing the resistance-current characteristics of semiconductor rectifiers.

A more specific object of my invention is improved methods and means of stabilizing the resistance-current characteristic defined as

$$I^{-a}=bR$$

of semiconductor-type rectifiers.

A still more specific object of my invention is methods and means of stabilizing the constants a and b in the characteristic

$$I^{-a}=bR$$

of germanium-type rectifiers.

Other objects of my invention and its true scope will appear as the following description of one embodiment

of my invention proceeds. In the accompanying drawings:

Fig. 1 shows the effective forward resistance characteristic of typical semiconductor rectifiers,

Fig. 2 is a graph showing how the effective resistance of a rectifier varies with current for different values of the constant b, and

Fig. 3 is a graph showing how the effective resistance of a rectifier varies with current for different values of the exponent a.

I have found that the resistance of a semiconductor rectifier varies with the forward current through the rectifier. The typical effective resistance-current characteristic of commercial rectifiers are represented by the curves of Figs. 2 and 3. Unfortunately, the current does not vary linearly with resistance but varies exponentially and suggests that the current-to-effective resistance relationship may be defined by the expression

$$I^{-a}=bR$$

where I and R are, respectively, current and effective resistance and where a and b are constants. If the value of the exponent a varies in use the curvature of the characteristic curve will change as suggested in Fig. 3, in which case circuitry containing the rectifier becomes unbalanced and decalibrated. It is particularly troublesome having dissimilar a values cross as in Fig. 3.

Effective resistance is defined to be that linear or ohmic resistance which will pass the same average current during a specified voltage pulse as will pass a non-linear rectifier when subjected to the same voltage pulse. It is likewise desirable that the constant b be stable during life so that the static parameters of the rectifier will not change and upset the circuitry in which it is incorporated.

It has been found that the conductivity of germanium may be changed when the crystals are bombarded by high-energy particles from a cyclotron. Bombarding the crystals appears to produce lattice dislocations and perhaps otherwise affect the electrical properties. I assumed, then, that the crystal structure and the position of the impurity atom might be changed with thermal-agitation, and I found this to be true when the crystals were heated. Although the electrical changes were small when the heat-induced energy of vibration was low, large changes occurred over long periods of time. The energy of vibration of an atom is increased as the temperature of the crystal is increased. It then became clear that exposing these germanium crystals to temperature fluctuations might accelerate the process of impurity migration to more stable locations.

On the assumption that alternately heating and cooling a germanium crystal containing suitable impurity molecules would tend to shift the molecules to more stable positions, I measured the effective forward resistance of a number of commercially available germanium rectifiers. Germanium rectifiers having effective forward resistances of the values indicated in Fig. 1 by curves 10 and 11, had an effective forward resistance of about 330 ohms when received from the manufacturer. As these particular rectifiers alternately were chilled to −60° C. and heated to +100° C., forward resistance continued to increase to 450 and 415 ohms, respectively, after four cycles of freezing and heating. Rectifiers with such widely variable forward resistances as these are obviously unsuited for commercial uses where the operating temperatures may be extreme. Other rectifiers such as those having the forward resistances indicated by curves 12, 13 and 14, on the other hand, decrease from an initial 440 ohms to values below 400 ohms as the crystal was subjected alternately to extreme high and low temperatures. Surprisingly, as the cycling of the crystal through extreme temperatures continued it was found that the forward

resistance changed less and less, percentage-wise. It seems reasonable to assume from these results that alternate heating and cooling of the semiconductor-type rectifier will stabilize its effective forward resistance-current characteristics.

In determining the range of temperatures to which the crystal must be subjected for adequate stabilization, expermentation indicated that the range may be quite narrow or quite wide. It was found that by heating and cooling to temperatures, respectively, above and below the range of temperatures to which the rectifiers would be subjected in use, the stabilization process could be accelerated. For some military purposes these ranges may vary from the temperatures of the tropics to the sub-zero temperatures of the polar regions. Norrower temperature operating ranges are of course usual. The maximum temperature to which a manufactured semiconductor rectifier can be subjected appears to be limited only by the temperature to which the glass-to-metal seals and other mechanical parts of the rectifier may be carried without damage. The minimum temperature to which the crystals may be frozen likewise is determined by the mechanical characteristics of the rectifiers. It was found, for example, that with some commercial rectifiers the difference in coefficient of expansion of the various parts may actually cause the contact electrode such as a cat whisker to separate from or shift on the crystal, or cause a fracture at the seals.

The number of heating-cooling cycles necessary to stabilize the forward resistance characteristic of the rectifier is likewise individual to each rectifier. The number of cycles in turn is dependent upon the magnitude of the temperature ranges employed. In the case of the rectifiers graphed in Fig. 1, about 18 cycles, using temperature extremes of −60° C. and +100° C., was considered satisfactory for sufficiently stabilizing the rectifiers for use in critically balanced circuits. No appreciable drift in the forward resistance of rectifiers thus processed has been noted after several months of use. The number of cycles of course may vary widely, the greater the number the greater being the invariability of the forward resistance.

Good results have been obtained when the crystals are heated to +100° C. and held at that temperature for 60 minutes and then refrigerated to −60° C. for about 60 minutes each, the crystals being held at room temperature for about 15 minutes between each heating and cooling excursion. As suggested above, when commercially available germanium rectifiers are thus treated for at least four cycles, the constants a and b in the resistance-current expression become sufficiently stable for many circuit applications. The constants a and b fluctuate less and less as the number of heating and cooling cycles increase.

Many modifications of my novel heating-cooling cycling may be made without departing from the scope of my invention. The time-temperature constant of each heat treatment, and the time-temperature constant of each cooling treatment should be sufficiently long, and the number of heating and cooling cycles should be sufficiently large that they render substantially invariable the constants a and b in the relationship

$$I^{-a}=bR$$

where I and R are the forward current and effective resistance, respectively, of the rectifier in the operating temperature range of the rectifier, and a and b are said constants.

Although the temperature cycling described and hereinafter claimed very probably produces the effects suggested relative to impurity location stabilization, it is to be understood that the utility of the method and the beneficial results which ensue may, in fact, be found in the future to be the result of other changes; for example, changes at the rectifying junction of the semiconductor, not clearly understood at the present state of the art.

I claim:

1. The method of treating a semiconductor-type rectifier having dissimilar metals in contact, said method comprising heating said rectifier to a temperature above the normal operating temperature of the rectifier, and then cooling said rectifier to a temperature below the normal operating temperature of the rectifier.

2. The method of treating a rectifier defined in claim 1 further comprising the step of holding the rectifier at substantially room temperature after the said heating excursion until the temperature of the rectifier substantially returns to room temperature.

3. The method of treating an assembled semiconductor-type rectifier to stabilize the effective forward resistance-current charactertistics of the rectifier comprising alternately heating and cooling said rectifier to temperatures outside the normal operating temperature range of said rectifier.

4. The method of accelerating the aging and resultant stabilization of the forward resistance-current characteristics of semiconductor rectifiers, comprising heating said rectifiers to approximately 100 degrees centigrade above zero and then cooling said rectifiers to approximately 60 degrees below zero, and repeating the mentioned heating and cooling steps a plurality of times.

5. In the method defined in claim 4, holding the rectifiers at each of the high and the low temperatures for approximately one hour.

6. In the method defined in claim 4, holding the rectifiers at room temperature for approximately one quarter hour between the heating and cooling excursions.

7. The method of stabilizing the resistance-current characteristic of an assembled semiconductor-type rectifier said characteristic being defined by the relationship, $I^{-a}=bR$, where R is resistance, I is current and a and b are constants, said process comprising alternately heating and cooling said rectifier to uncritical temperature extremes of about +100° C. and about −60° C. maintaining the said rectifier for about one hour at the temperature extreme of each of the said heating and cooling excursions, and continuing the heating and cooling excursions until said constant a reaches the desired degree of stabilization within a predetermined range of operating temperatures between the temperature extremes of the aforesaid heating and cooling excursions.

8. The method of stabilizing the resistance-current characteristic of an assembled semiconductor-type rectifier, said characteristic being defined by the relationship, $I^{-a}=bR$, where R is resistance, I is current and a and b are constants, said process comprising alternately heating and cooling said rectifier between about +100° C. and about −60° C. for about one hour for each heating and cooling excursion, and continuing the heating and cooling excursions for at least four cycles.

9. The method of stabilizing the resistance-current characteristic of an assembled semiconductor-type rectifier, said characteristic being defined by the relationship, $I^{-a}=bR$, where R is resistance, I is current and a and b are constants, said process comprising heating said rectifier to about +100° C., then cooling said rectifier to about −60° C., and repeating the heating and cooling until said constants reach a desired degree of stabilization for a given temperature.

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