Dec. 24, 1957 J. I. PANKOVE 2,817,608

MELT-QUENCH METHOD OF MAKING TRANSISTOR DEVICES

Filed May 2, 1955

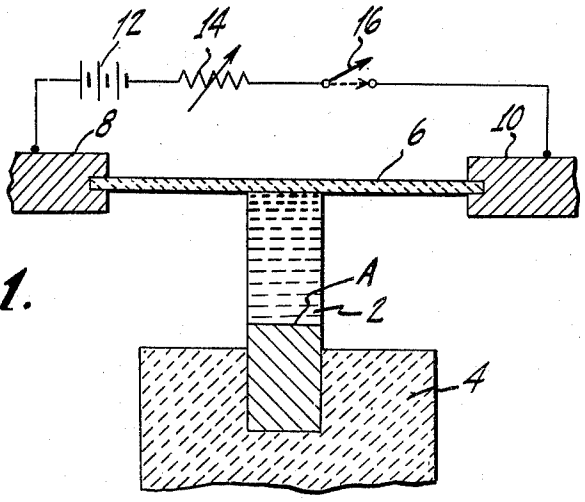


Fig. 1.

Fig. 2.

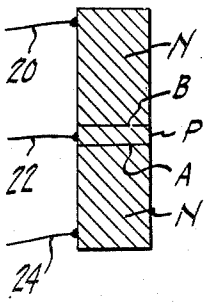
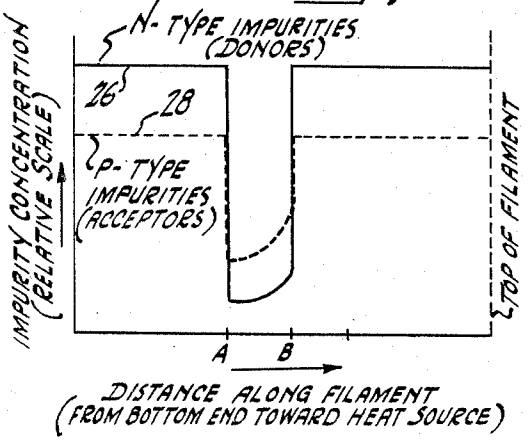


Fig. 3.



INVENTOR.
JACQUES I. PANKOVE
BY J. L. Whittaker
ATTORNEY

United States Patent Office 2,817,608
Patented Dec. 24, 1957

2,817,608

MELT-QUENCH METHOD OF MAKING TRANSISTOR DEVICES

Jacques I. Pankove, Princeton, N. J., assignor to Radio Corporation of America, a corporation of Delaware

Application May 2, 1955, Serial No. 505,333

7 Claims. (Cl. 148—1.5)

This invention relates generally to improved methods of making semiconductor devices. More particularly, it relates to improved methods of making filamentary type transistors having a plurality of rectifying barriers which divide the filaments electrically into a plurality of separate zones.

An object of the invention is to provide improved methods for making improved semiconductor rectifying devices.

Another object is to improve rectifying barriers in semiconductor devices.

A further object is to simplify and improve the fabrication of semiconductor devices.

The instant invention is an improvement over the process described by W. G. Pfann in the Journal of Metals for February 1954, pages 294 et seq. Pfann describes the formation of two spaced rectifying barriers in a germanium semiconductor body doped with two different impurities capable of imparting opposite conductivity types to the semiconductor, by first melting and then slowly refreezing a portion of the body.

According to the instant invention it has been found that unexpected improvements in the electrical properties of devices produced by melting and refreezing portions of semiconductor bodies are provided by radically changing the rate of refreezing taught by Pfann. Whereas Pfann teaches melting and subsequent slow refreezing, applicant has found unexpected advantages in melting and subsequently refreezing at a rapid rate as hereinafter described.

The semiconductor bodies treated according to the invention to form transistor devices are most conveniently filamentary in form. They initially include evenly distributed impurities of both donor and acceptor types. The impurities of the type present in the greater numbers are selected to have a smaller segregation coefficient in the semiconductive body than the impurities of the opposite type. According to the instant invention such a filament is melted from one end partially along its length and then quenched by rapidly refreezing it at a minimum initial cooling rate of at least 500° C. per second. The melting and quenching produces a pair of closely spaced rectifying barriers within the filament closely adjacent to the interface between the molten and solid portions of the filament.

The invention will be explained in greater detail in connection with the accompanying drawing of which:

Figure 1 is a schematic, cross-sectional, elevational view of a semiconductor filament being processed according to the invention; and

Figure 2 is a schematic, cross-sectional, elevational view of a semiconductor filament after treatment according to the invention to form it into a transistor; and

Figure 3 is a line graph describing the distribution of donor and acceptor impurities along the length of the filament shown in Figure 2.

Similar reference characters are applied to similar elements throughout the drawing.

The process of the invention makes use of the resegregation effect. This effect is explained in detail in the

article heretofore referred to and in an article, also by Pfann, in the Journal of Metals, p. 861, for August 1952.

The segregation effect concerns the relative solubilities of solutes in the molten and liquid phases respectively of a freezing solvent. In germanium and silicon, for example, most solutes are more soluble in the liquid phase than the solid. The quantitative expression for the effect is called the segregation coefficient. The segregation coefficient of an impurity substance in germanium, for example, may be defined as the ratio of the concentration of the impurity substance on the solid side of the interface of a growing ingot of freezing germanium to the concentration on the liquid side of the interface. (Concentration in solid ÷ concentration in liquid.) When two different impurities are present in a freezing system in relatively small proportions they act substantially independently of each other with respect to the segregation effect.

Referring now to Figure 1, a transistor device may be made according to a preferred embodiment of the invention utilizing a filament **2** of n-type single crystal semiconductive germanium. The filament may be, for example, about 0.10" long and about .03" in diameter. It includes both donor and acceptor impurities, the donor, or n-type impurities being present in larger quantity than the acceptor, or p-type impurities. Further, the donor impurities are selected to have a substantially smaller segregation coefficient in germanium than the acceptor impurities. The impurities may consist of dispersed atoms of respectively, gallium (an acceptor impurity having a segregation coefficient of 0.1) and antimony (a donor impurity having a segregation coefficient of .005). The gallium may be present in a quantity of about 4×10^{16} atoms per cc. in the germanium and the antimony may be present in a quantity of about 5×10^{16} atoms per cc. Both impurities are substantially uniformly distributed throughout the filament. The antimony, therefore, is the predominant impurity and determines the conductivity type of the germanium.

The filament is held vertically in a well in a graphite or stainless steel block **4** which has a relatively large thermal capacity and acts as a heat sink. One end of the filament is brought into contact with a flat carbon or tantalum wire **6** in a non-oxidizing atmosphere such as helium or hydrogen. The wire is held by a pair of contact electrodes **8** and **10** and electrically connected in series with an electric current source **12** through a control resistor **14** and a switch **16**. After the germanium filament contacts the wire the switch is turned on to allow an electric current to flow through the wire to heat it to about 2200° to 2800° C. The current flow is maintained for about one second during which time heat is transferred from the wire to the germanium filament to melt approximately half the length of the filament. The supporting block **4** cools the bottom portion of the filament which is remote from the wire and prevents the wire from melting the entire filament. After about one second the switch is opened and the filament is allowed to cool rapidly down to room temperature. The initial rate of cooling is about 1000° C. per second.

The above described process produces a filamentary body with two closely spaced p-n rectifying junctions A and B disposed transversely across the filament as shown in Figure 2. Both the junctions are formed in relatively abrupt transition zones, or regions between the n-type and p-type portions of the body. One junction (A) is formed at the surface corresponding to the interface between the molten and solid portions of the filament at the point of its farthest advance. This junction is similar to one of the junctions described by Pfann. A second rectifying junction (B) is formed closely adjacent to the first and substantially parallel to it.

The filament is thus divided electrically into three separate regions. The end portions of the filament are of n-type conductivity and a central, relatively narrow portion is of p-type conductivity.

The filament may then be etched according to any of several known techniques to delineate the central, p-type conductivity region upon its surface. Electrical leads 20, 22 and 24 may then be attached to the respective regions of the device and the device may be conventionally mounted and potted.

The central p-type conductivity region becomes the base region when the device is utilized as an n-p-n transistor. It is relatively flat and its thickness may be less than .001". This central region can be conveniently located at about the middle of the filament. An electrical connection forming the transistor base connection may be made to this region by any conventional process such as by surface alloying an indium electrode or by the gold-bonding technique utilizing gold alloyed with an acceptor impurity. Such connections are substantially non-rectifying, or ohmic with respect to the p-type conductivity region. They form p-n rectifying barriers, however, upon n-type conductivity material. Thus if the junction between a gold bonded lead and the filament extends beyond the edge of the p-type region and contacts the n-type region it does not electrically short-circuit the barrier between the regions. The only effect of such an extension is a corresponding extension, or deformation of the base region to include the entire contact area of the gold bonded lead.

The leads 24 and 20 connected to the n-type end portions of the filament may be soldered thereto by, for example, a tin-lead solder with which is alloyed a small percentage of a donor impurity such as antimony.

The line graph of Figure 3 illustrates the resegregation effect in the practice of the invention with respect to the embodiment heretofore described. The two lines 26 and 28 represent respectively, the donor, or n-type impurity concentration and the acceptor, or p-type impurity concentration at consecutive planes along the length of the filament. The origin of the graph corresponds to the end of the filament seated in the heat sink.

During the process the impurities in the solid, unmelted portion of the filament remain substantially unchanged and in their original concentrations. Here the donor impurities predominate and the filament is of n-type conductivity. The filament is melted during the process from its top down to the plane represented by the point A in the graph. When the heat supplied to the filament is cut off there is initially a relatively brief time during which the filament cools and freezes longitudinally at a relatively slow rate such that the resegregation effect is operative. This brief time is believed to be closely related to the time necessary to cool the molten portion of the filament to a temperature close to its freezing point. After this brief time the remainder of the filament freezes so rapidly that the impurities present in the freezing portion are not resegregated but are quenched in position.

Most of the heat dissipation during cooling is by conduction through the solid portion of the filament and into the heat sink. A consideration of the parameters involved reveals that relatively little heat is lost by radiation and by gas convection directly from the filament into the surrounding space. There results, therefore, a thermal gradient extending along the length of the filament from the heated end toward the heat sink. This gradient induces longitudinal freezing which is believed to be a primary factor in causing the filament to refreeze in single crystal form determined by the crystal lattice orientation of the non-melted portion.

During the time that the resegregation effect is operative, a portion of the filament corresponding to the increment A to B in the line graph is frozen. The relative concentrations of the two impurities in this region are affected by their respective segregation characteristics. Since the donor, or n-type impurity has a relatively small segregation coefficient, relatively small proportions of it are included in this region. The acceptor, or p-type impurity, on the other hand, has a relatively large segregation coefficient and relatively large proportions of it are included in the region.

The quantities of the two impurities initially provided in the filament are selected with respect to their segregation coefficients so that even though the donor impurity is present in a larger quantity than the acceptor, it will be included in a smaller quantity in the resegregated portion of the filament. Mathematically, the required relationships regarding the impurities initially present in the filament may be expressed as follows:

$$C_d > C_a > \frac{k_d C_d}{k_a}$$

where:

k_a is the segregation coefficient of the acceptor impurity
k_d is the segregation coefficient of the donor impurity
C_a is the concentration of the acceptor impurity
C_d is the concentration of the donor impurity

For optimum electrical characteristics it is also desirable that k_a be as much greater than k_d as possible. This permits a maximum difference in conductivities between the end portions of the filament and the resegregated portion, which difference is conducive to desirable transistor characteristics.

By suitably selecting the impurities initially present in the filament and their respective concentrations the resistivities of the different regions after processing may be controlled within relatively wide limits. For example, the filament may initially include a relatively low concentration of boron, a donor impurity having a large segregation coefficient, and a relatively high concentration of bismuth, an acceptor impurity having a small segregation coefficient. The relative concentrations of these two impurities may be selected to provide a relatively low resistivity in the end portions of the filament by making the bismuth concentration greatly exceed the boron concentration. Simultaneously, the resegregated, central portion of the filament is caused to have a relatively high resistivity since after resegregation the boron concentration exceeds the bimuth concentration by only a small margin.

After the resegregated portion of the filament is frozen, the remainder of the filament freezes so rapidly that the resegregation effect is ineffective and the impurities are present throughout the remainder of the filament in substantially their original concentrations. In the end portions of the filament where the donor impurity concentration exceeds the acceptor impurity concentration, the filament exhibits n-type conductivity, and in that portion of the filament where the acceptor concentration exceeds the donor concentration, the filament exhibits p-type conductivity. The respective consecutive portions of the filament are electrically separated by p-n rectifying barriers.

One important advantage of the invention is the provision of two closely spaced p-n rectifying junctions in a semiconductive filament, each of which junction lies within a relatively abrupt transition zone between a p-type conductivity region and an n-type conductivity region. Such a structure is particularly desirable as a symmetrical transistor for use in devices such as electronic switches and reversible amplifiers.

Another advantage is the relative ease and rapidity with which transistor devices may be made. The entire process takes no more than a few seconds. Further, the process of the invention is not subject to critical tolerance limitations. For example, the length of the filament that need be melted is not critical since this factor affects pri-

marily only the specific location along the length of the filament at which the two rectifying junctions are formed. The temperature of heating, also, is not critical since the melting process appears to attain thermal equilibrium. The length of the portion of the filament that is melted is determined by the amount of heat provided, while the heat sink maintains one end of the filament at a temperature well below its melting point and prevents the melting of the entire filament.

The time factor is believed to be primarily responsible for the lack of deformation of the melted portion of the filament. If the heat is applied too long while the material is melted, surface tension forces may cause the molten material to ball up at the end of the filament. In this case the cooling part of the process is less uniform and non-planar or non-uniform rectifying barriers may be formed. It is preferred, therefore, to start cooling immediately after the heated end of the filament attains the desired temperature of 1500° to 2000° C.

In making practicable devices the principal critical factor appears to be the spacing between the two junctions. The spacing is affected primarily by the rate of cooling of the device after the heating is removed. A rapid rate of cooling provides closely spaced junctions, whereas a relatively slow rate of cooling provides relatively widely spaced junctions. In either case, however, the rate of cooling is extremely rapid when judged by the rates of cooling previously employed in the manufacture of semiconductor devices and materials.

One way to control the rate of cooling is to vary the temperature of the heat sink to control the thermal gradient along the filament. It has been found that convection and radiation heat losses are of only minor importance in determining the rate of cooling of the filament. The principal heat loss is by conduction through the filament to the heat sink. The heat sink may be cooled, for example, by directing a stream of cool water or liquid nitrogen through it to increase the thermal gradient along the filament, thereby to increase the cooling rate to minimize the spacing between the two junctions.

In order to ensure an abrupt transition zone at the second formed junctions, it is necessary to quench the end portion of the filament. Otherwise, the resegregation effect proceeds along the length of the filament as shown by Pfann and produces a gradual transition zone. The quenching is also highly desirable in order to provide close spacing between the two junctions without placing both of them critically close to one end of the filament.

If the filament is melted and subsequently slowly refrozen, it has been found that either the two junctions must be widely spaced or formed very close to the melted end of the filament. If the two junctions are formed by slow freezing sufficiently close together to provide desirable electrical characteristics at relatively high frequencies they must be formed so close to the end of the filament that any contact made to the end of the filament is apt to damage or to interfere with the junction adjacent thereto. According to the invention, filamentary transistors may be made having pairs of p-n rectifying junctions closely spaced and extending transversely across the filaments at any desired locations along the lengths of the filaments.

It has previously been thought that the growth of a single crystal of semiconductive materials such as germanium and silicon depended to a large extent upon a slow rate of cooling. According to the instant invention, however, it has been unexpectedly discovered that even when quenched at the extremely rapid cooling rates heretofore described, partially melted filaments of semiconductive germanium and silicon refreeze in substantially single crystal form.

To provide uniform characteristics among successive

devices and to provide optimum characteristics in semiconductor devices such as transistors generally, it has been found that each of the devices must comprise a single crystal of semiconductive material. If any portion of a device such as the transistor illustrated in Figure 2, for example, is crystallographically inhomogeneous the electrical characteristics of the device are apt to be inferior, unpredictable and very possibly variable with time.

The practice of the invention is, of course, not limited to a specific device incorporating the specific materials heretofore described. For example, devices similar to the one shown in the drawing may be made utilizing semiconductive silicon or an alloy of silicon and germanium. Also, the particular impurities and their concentration may be varied according to the principles heretofore set forth to produce p-n-p as well as n-p-n devices. That is, an acceptor impurity having a small segregation coefficient may be initially included in the filament as the dominant impurity in conjunction with a donor impurity having a relatively large segregation coefficient. Then:

$$C_a > C_d > \frac{k_a C_a}{k_d}$$

is the required relationship between the impurities initially in the filament.

A partial list of impurities that may be used in conjunction with semiconductive germanium and silicon according to the principles of the invention is set out below. The segregation coefficients listed are those with respect to germanium and are empirical. They are determined for a slow rate of freezing such as utilized in the freezing of the resegregated portion of a filament according to the invention. The figures given may be used as a guide in selecting significant impurities for the purpose of the invention. The respective coefficients for the listed materials in silicon are directly proportional to the coefficients in germanium.

Donor Impurities	k_{Ge}	Acceptor Impurities	k_{Ge}
Phosphorus	0.12	Boron	3
Arsenic	.06	Gallium	0.1
Antimony	.005	Aluminum	0.1
Bismuth	.0001	Zinc	.01
		Indium	.001

There have thus been described improved methods of making filamentary, junction type transistors by a "melt-quench" process in which a longitudinal portion of a filamentary crystal of a semiconductive material is melted and then rapidly refrozen to form a pair of spaced, parallel, planar p-n rectifying barriers in the crystal.

What is claimed is:

1. Method of making a semiconductor device comprising the steps of melting throughout the entire thickness a longitudinal portion of a crystalline semi-conductive filament, said filament including both acceptor and donor conductivity type-determining impurities in relative proportions such that the following relationship is satisfied:

$$C_x > C_y > \frac{k_x C_x}{k_y}$$

where

C_x is the atomic concentration of said impurities of one type,

C_y is the atomic concentration of said impurities of the opposite type,

k_x is the segregation coefficient of said impurities of said one type in said filament, and

k_y is the segregation coefficient of said impurities of said opposite type in said filament,

maintaining another longitudinal portion of said filament in its solid state, and subsequently quenching said melted portion by rapidly refreezing it at a minimum initial cool-

ing rate of at least 500° C. per second so that solidification starts at the unmelted cool end and proceeds to the other end, thereby to form a pair of spaced parallel p-n rectifying barriers in said filament.

2. Method of making a semiconductor device comprising the steps of melting throughout the entire thickness a longitudinal portion of a single crystal semi-conductive filament by applying heat at one end of said filament, said filament including both acceptor and donor conductivity type-determining impurities in relative proportions such that the following relationship is satisfied:

$$C_x > C_y > \frac{k_x C_x}{k_y}$$

where

C_x is the atomic concentration of said impurities of one type,

C_y is the atomic concentration of said impurities of the opposite type,

k_x is the segregation coefficient of said impurities of said one type in said filament, and

k_y is the segregation coefficient of said impurities of said opposite type in said filament,

maintaining another longitudinal portion of said filament at the opposite end thereof from said one end in its solid state at a temperature below its melting point thereby to establish a thermal gradient along the length of said filament, and subsequently quenching said melted portion by rapidly extracting heat from said solid portion at an initial rate of at least 500° C. per second thereby to maintain said thermal gradient and to cause said melted portion to freeze longitudinally starting at the unmelted cool end and proceeding to the other melted end to form a pair of spaced parallel p-n rectifying barriers in said filament.

3. Method of making a semiconductor device comprising the steps of melting a longitudinal portion of a single crystal semiconductive filament throughout its entire thickness by applying heat at one end of said filament, said filament including both acceptor and donor conductivity type-determining impurities in relative proportions such that the following relationship is satisfied:

$$C_x > C_y > \frac{k_x C_x}{k_y}$$

where

C_x is the atomic concentration of said impurities of one type,

C_y is the atomic concentration of said impurities of the opposite type,

k_x is the segregation coefficient of said impurities of said one type in said filament, and

k_y is the segregation coefficient of said impurities of said opposite type in said filament,

maintaining another longitudinal portion of said filament at the opposite end thereof from said one end in its solid state at a temperature below its melting point thereby to establish a thermal gradient along the length of said filament, and subsequently quenching said melted portion by rapidly extracting heat from said solid portion at a rate sufficient to provide an initial cooling rate of at least 500° C. per second in the molten portion of said filament thereby to maintain said thermal gradient and to cause said melted portion to freeze longitudinally starting at the unmelted cool end and proceeding to the other end to form a pair of spaced parallel p-n rectifying barriers in said filament.

4. Method of making a semiconductor device comprising the steps of melting a longitudinal portion of a single crystal semiconductive germanium filament throughout its entire thickness by applying heat at one end thereof, said filament including both acceptor and donor conductivity type-determining impurities in relative proportions such that the following relationship is satisfied:

$$C_a > C_d > \frac{k_a C_a}{k_d}$$

where

C_a is the atomic concentration of said acceptor impurities,

C_d is the atomic concentration of said donor impurities,

k_a is the segregation coefficient of said acceptor impurities in germanium, and

k_d is the segregation coefficient of said donor impurities in germanium,

maintaining another longitudinal portion of said filament at the opposite end of said filament from said one end in its solid state at a temperature below its melting point, and subsequently quenching said melted portion by cooling it at a minimum initial cooling rate of 500° C. per second so that solidification starts at the unmelted cool end and proceeds to the other end, thereby to form a pair of spaced parallel p-n rectifying barriers in said filament.

5. Method of making a semiconductor device comprising the steps of melting a longitudinal portions of a single crystal semiconductive germanium filament throughout its entire thickness by applying heat at one end thereof, said filament including both acceptor and donor conductivity type-determining impurities in relative proportions such that the following relationship is satisfied:

$$C_d > C_a > \frac{k_d C_d}{k_a}$$

where

C_a is the atomic concentration of said acceptor impurities,

C_d is the atomic concentration of said donor impurities,

k_a is the segregation coefficient of said acceptor impurities in germanium, and

k_d is the segregation coefficient of said donor impurities in germanium,

maintaining another longitudinal portion of said filament at the opposite end of said filament from said one end in its solid state at a temperature below its melting point, and subsequently quenching said melted portion by cooling it at a minimum initial cooling rate of 500° C. per second so that solidification starts at the unmelted cool end and proceeds to the other end, thereby to form a pair of spaced parallel p-n rectifying barriers in said filament.

6. Method of making a semiconductor device comprising the steps of melting a longitudinal portion of a single crystal semiconductive germanium filament throughout its entire thickness by applying heat at one end of said filament in a non-oxidizing atmosphere, said filament including dispersed atoms of gallium and antimony, the antimony atoms being present in a greater number than the gallium atoms, the number of gallium atoms being greater than $\frac{1}{20}$ the number of antimony atoms, maintaining another longitudinal portion of said filament at the opposite end thereof from said one end in its solid state at a temperature below its melting point, and subsequently quenching said melted portion at a minimum initial cooling rate of 500° C. per second so that solidification starts at the unmelted cool end and proceeds to the other end, thereby to form a pair of spacel parallel p-n rectifying barriers in said filament.

7. Method of making a semiconductor device comprising the steps of melting a longitudinal portion of a single crystal semiconductive germanium filament throughout its entire thickness by applying heat at one end of said filament in a non-oxidizing atmosphere, said filament including dispersed atoms of gallium and antimony, the antimony atoms being present in a greater number than the gallium

atoms, the number of gallium atoms being greater than 1/20 the number of antimony atoms, maintaining another longitudinal portion of said filament at the opposite end of said filament from said one end in its solid state at a temperature below its melting point thereby to establish a thermal gradient along the length of said filament, and subsequently quenching said melted portion at a minimum initial cooling rate of 500° C. per second by extracting heat from said solid portion thereby to maintain a thermal gradient along the length of said filament to cause said melted portion to freeze longitudinally so that solidification starts at the unmelted cool end and proceeds to the other end in single crystal form as determined by the crystal lattice of said solid portion, and to form a pair of spaced parallel p-n rectifying barriers in said filament.

References Cited in the file of this patent

UNITED STATES PATENTS

2,739,088 Pfann ---------- Mar. 20, 1956

FOREIGN PATENTS

1,065,523 France ---------- Jan. 13, 1954