

June 24, 1958

R. G. TREUTING

2,840,495

METHOD OF PROCESSING SEMICONDUCTIVE MATERIALS

Filed Aug. 21, 1953

2 Sheets-Sheet 1

FIG. 1

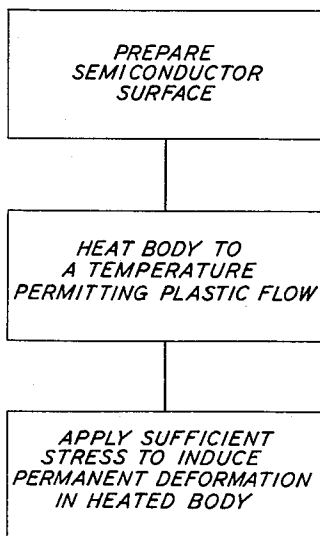


FIG. 4

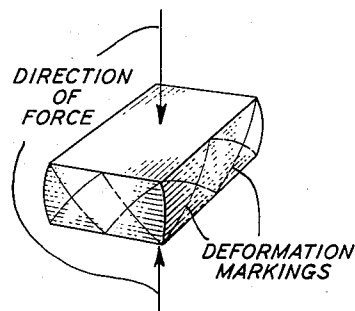


FIG. 2

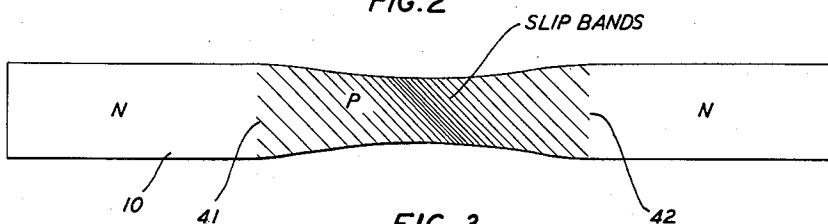
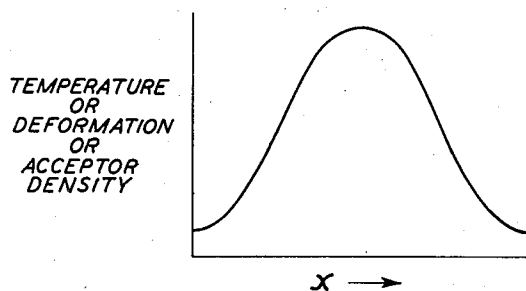


FIG. 3



INVENTOR
R. G. TREUTING
BY David H. Wilson
ATTORNEY

June 24, 1958

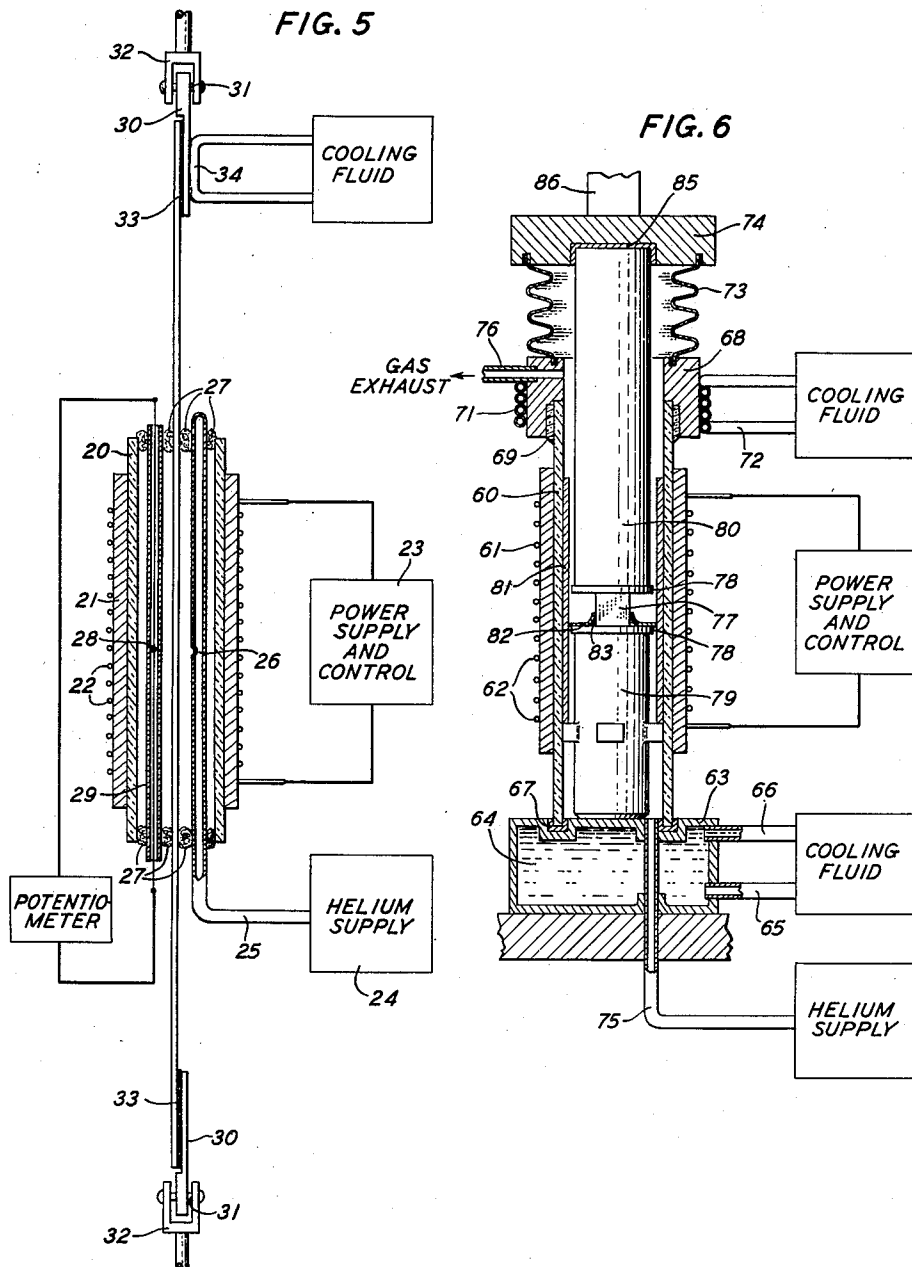
R. G. TREUTING

2,840,495

METHOD OF PROCESSING SEMICONDUCTIVE MATERIALS

Filed Aug. 21, 1953

2 Sheets-Sheet 2



INVENTOR
R. G. TREUTING
BY *David H. Wilson*
ATTORNEY

1

2,840,495

METHOD OF PROCESSING SEMICONDUCTIVE MATERIALS

Robert G. Treuting, Chatham Township, Morris County, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application August 21, 1953, Serial No. 375,788

4 Claims. (Cl. 148—1.5)

This invention relates to methods of treating semiconductive materials and more particularly to methods of altering the electrical characteristics of germanium and silicon.

Objects of the invention are to facilitate the processing of semiconductive materials, to enable a control of the balance of acceptor and donor centers to be effected, to convert semiconductive material from n- to p-conductivity type, and to produce semiconductive bodies having p-n junctions.

A feature of the invention resides in permanently deforming semiconductive materials, for example germanium or silicon, by heating bodies of the materials and applying a stress to them whereby lattice defects are produced which alter the effective difference of acceptor and donor centers present therein. The lattice defects introduced by this technique may be characterized as any localized perturbation of the regular crystal structure consequential to plastic deformation, for example a dislocation.

Another feature resides in permanently deforming n-type semiconductive materials of about 1 ohm centimeter resistivity or more by stressing them at temperatures several hundred degrees below their melting point to convert the material to p-conductivity type.

Another feature resides in producing n-p junctions in silicon and germanium by permanently deforming one portion of a semiconductive body containing a donor predominance, n-type, to a degree which introduces an acceptor predominance while limiting the deformation in an adjacent contacting portion of the body to a level which introduces an insufficient shift in the donor-acceptor balance to overcome the initial donor predominance.

Germanium and silicon in the pure state have an atomic structure of the diamond cubic lattice form wherein each of the four valence electrons of each atom forms an electron pair bond with one of the four valence electrons of each of four adjacent atoms. Conduction in these semiconductive materials is effected by defects in the electron pair bonds. Thus, mechanisms may be present in the crystal structure which provide loosely bound electrons which can be moved through the crystal structure by the application of only small amounts of energy to carry a negative charge through the material. Materials having free negative charge carriers are termed "n-conductivity type semiconductors" and the mechanism supplying the loosely bound electron is termed a "donor" or a "donor center." Similarly an electron deficit in the crystal structure can be made to move therethrough to effect a flow of positive charge. Materials having these positive charge carriers, termed "holes," are identified as "p-type semiconductors" and the mechanism supplying the hole is termed an "acceptor" or an "acceptor center." Electrons in proximity to holes tend to recombine with those holes to effect the mutual annihilation of both forms of carriers. Thus acceptors and donors compensate for

2

each other's presence and the conductivity type which a semiconductor exhibits depends upon which predominates.

Acceptors and donors are attributable to several mechanisms. They are produced by the presence of impurities which fit into the crystal structure substitutionally for the semiconductor atoms and have other than the four valence electrons required to form the electron pair bonds of a semiconductor atom. For example, certain elements of group 3 of the periodic table such as aluminum, gallium, and indium form acceptors in silicon and germanium since they each supply only three of the four valence electrons necessary to complete the crystal structure and thus establish a hole in the material. Phosphorous, arsenic, antimony, and bismuth of group five of the periodic table each supply an excess valence electron and are donors in the crystal structure. It has also been suggested that crystal structure imperfections introduce donors and acceptors. Thus, a polycrystalline body of semiconductive material may contain crystal interfaces on each side of which are incomplete electron pair bonds which function as acceptor centers. Similarly vacant lattice sites may be present to act as acceptor centers.

In accordance with a feature of this invention, acceptor centers are introduced in semiconductive material by permanently deforming it. The plastic deformation of germanium and silicon introduces dislocations which act as a source of acceptor centers. The calculation of the number of dislocations in deformed material from its structure, and of the number of introduced acceptor centers from its resistivity indicate that one acceptor center is introduced at each point of intersection of a dislocation line with the crystal planes normal thereto. At each intersection the valence requirements of the germanium atom, unsatisfied because of the discontinuity in the crystal structure, are satisfied by accepting an electron from the valence band. This mechanism generates a hole carrier.

Since the conductivity type of a semiconductor depends upon the type of carrier which predominates, the introduction of acceptor centers in a material may be said to render it more p-type, i. e. its n-type resistivity increases, with the further introduction of acceptor centers it converts to high resistivity p-type, and with the still further introduction of acceptor centers becomes low resistivity p-type. The number of acceptor centers introduced increases with the amount of plastic deformation. It follows, therefore, that within limits there exists a degree of deformation which will accomplish conversion of n-type material to p-type.

It has been found that germanium can be deformed under conditions which introduce a sufficient number of acceptor centers to effect the conversion of material having initial donor predominances corresponding to n-type resistivities of about 1 ohm centimeter or greater. One limit on the introduction of acceptor centers is set by the degree of deformation possible in the material. Germanium has been deformed about 56 percent, and the calculated number of introduced acceptor centers has been of the order of 10^{15} . In order to obtain practical levels of plastic or permanent deformation in germanium and silicon it is necessary that the deforming stress be applied at an elevated temperature. The minimum temperature at which a practical degree of deformation is realized is about 500° C. for germanium and 725° C. for silicon or about 60 percent of the absolute melting temperature. Another consideration is that germanium and silicon strain harden and this strain hardening reaches a magnitude which prevents further deformation sooner at low temperatures than at high temperatures. Since the ma-

terial also flows more readily at higher temperatures, it would appear advantageous to stress the material near its melting point. However, another factor sets upper limits on the temperature for deformation where the process is employed to make the semiconductor more p-type.

A limit is set on the number of acceptor centers introduced by a given degree of deformation by the time and temperature incident to deforming. When a silicon or germanium body is subjected to increased temperature and/or longer heating cycles, a relaxation occurs in the crystal structure which decreases the net number of acceptor centers present. This relaxation is structurally evidenced by a polygonization attributable to the diffusion of dislocations from an approximately random distribution to an array constituting the small angle boundaries of polygonization. The effect of this diffusion of dislocations appears to result in one or more of the following reactions which are evidenced by an effective increase in the donor predominance in materials deformed above the heating cycle time-temperature limit: an interaction between dislocations of opposite sign with a resultant mutual annihilation as acceptor centers, an interaction between dislocations and lattice vacancies to displace the dislocation by one lattice plane and remove the vacancy as an acceptor center, or an interaction between the dislocations and a solute atom to fix such an atom in the dislocation field and satisfy more fully the valence requirements of the semiconductor atom at the dislocation, thus cancelling it as an acceptor center.

Another consideration influencing the choice of upper limits of temperature and time of heating cycle is the thermal introduction of acceptors as disclosed in Patent 2,602,763 which issued July 8, 1952, to J. H. Scaff and H. C. Theuerer. The introduction of these acceptors can be inhibited by special processing techniques as set forth, for example, in the application of R. A. Logan and M. Sparks, Serial No. 334,972, filed February 3, 1953, now U. S. Patent No. 2,698,780. However, even with such treatments it is found advantageous to practice the process of this invention at low temperatures and for short heating cycles, e. g. below about 650° C. for germanium.

As will be illustrated below, within the heating cycle limits of this process the plastic deformation of silicon and germanium renders its conductivity less n- and more p-type to a greater extent than in an undeformed, similarly prepared and heat treated specimen. The upper limits of the heating cycle are evidenced by a reversal of this effect wherein the deformed material is less p-type than the undeformed material. These limits occur at about 92 percent of the melting temperature of the material on the absolute scale, e. g. at about 850° C. for germanium.

Since it is desirable that the material into which acceptor centers are introduced be homogeneous in the interest of producing reproducible and controlled deformation and electrical characteristics, the material treated is advantageously initially a single crystal. Single crystals produced by drawing a seed from a melt or by zone melting can be employed advantageously.

This invention, its objects and its features will be more fully understood from the following detailed description when read in conjunction with the accompanying drawings in which:

Fig. 1 is a flow chart setting forth the steps of the invention;

Fig. 2 is an elevation of a bar of semiconductive material permanently deformed in tension;

Fig. 3 represents the temperature distribution, deformation, and density of acceptor centers introduced by deformation along the heated portion of the specimen shown in Fig. 2;

Fig. 4 is a perspective of a semiconductive specimen permanently deformed in compression;

Fig. 5 is a sectioned schematic elevation of the apparatus employed in deforming the specimen of Fig. 2; and

Fig. 6 is a sectioned schematic elevation of the apparatus employed in compressively deforming specimens.

Referring now to the drawings, Fig. 1 outlines the principal steps involved in the process of this invention. The deformation imposed by this process may be of any form.

A typical tensile stressed specimen 10 is depicted in Fig. 2. It comprised a single crystal rod having a growth in approximately a $\langle 221 \rangle$ direction and an n-type resistivity of about 10 ohm centimeters over the three inch length deformed. The rod 10 was cut to .050" x .200" x 8", polished in an etchant composed of 15 parts by volume of acetic acid, 25 parts by volume of nitric acid (1.42 specific gravity), 15 parts by volume of hydrofluoric acid (48 percent), and sufficient liquid bromine to saturate the mixture. It was then mounted in the apparatus to be described below and heated at a maximum temperature of about 750° C. while subjected to a maximum tensile stress along the direction of growth of 2300 pounds per square inch. The maximum deformation was about 8 percent and occurred at the hottest point in the furnace, while the average deformation over the length within the furnace was about 4.8 percent. The resistivity of the deformed material ranged from 30 to 50 ohm centimeters p-type. Curves representative of the distributions of temperature, deformation, and introduced acceptor centers are presented in Fig. 3. The furnace is of such construction that the gradient in the temperature of that portion of the specimen within it was from about 750° C. at the longitudinal center to about 100° C. at the ends of the inner tube. The distribution of deformation followed the temperature gradient so that deformation was concentrated at that portion of the sample heated to the highest temperature.

The distribution of deformation is also illustrated in Fig. 2 by the representation of slip bands, i. e. slip line centers visible to the unaided eye, which are highly concentrated in the region subjected to the greatest temperature and more widely separated in the regions which were cooler. The heat treating cycle of the illustrative specimen at the center of the furnace was as follows: the temperature was raised at an approximately inverse exponential rate to 750° C. over an interval of 20 minutes, that temperature was maintained for 2½ minutes while the stress was applied and was cooled to 100° C. over an interval of 30 minutes along an exponential type of curve, the initial cooling rate being quite rapid as compared to the rate during the latter portion of the cooling interval.

The apparatus for performing a tensile deformation is shown in Fig. 5. It comprises a vertical, fused silica, tube furnace 20 mounted within a ceramic tube 21 on which is wound a resistance heater 22. The heater is supplied from a suitable power source through a controller as represented at 23 to provide a temperature distribution within tube 20 of the form shown by the curve of Fig. 3. The atmosphere within the hot zone should be such as to prevent any chemical reaction on the semiconductor surface, for example helium, argon, or nitrogen might be employed. Gas is supplied to the furnace interior from supply 24 through pipe 25 having its exit 26 at the longitudinal center of the furnace. The gas is supplied at a pressure slightly in excess of atmospheric, flows from aperture 26 without any marked directivity, and flows from the furnace at both ends through loose plugs 27 of asbestos paper surrounding the specimen where it projects from the furnace. Temperature monitoring may be realized by means of a thermocouple such as the chromel-alumel couple 28 located at the longitudinal center of the furnace within a protective tube 29 of fused silica. This thermocouple 28 can be associated with a potentiometer or a recorder-controller to facilitate control of the furnace temperature.

In stressing a specimen in tension it may be secured to suitable grips by soft solder. As may be seen in Fig.

5 a grip 30 can be formed from a member having a flat face to which the specimen is soldered 33 and an extension through which it can be pinned 31 to conventional machine grips 32. Inasmuch as considerable convection heating of the upper portion of the specimen occurs, it is advantageous to provide means for cooling the upper grip for example by brazing a cooling tube 34 to the face of the grip opposite that to which the specimen is soldered and by passing a suitable cooling fluid through it during the heating cycle.

It will be noted that in the apparatus of Fig. 5 only a portion of the specimen is heated to a temperature which permits plastic flow to occur, accordingly, only that heated portion of the specimen is deformed. Since conversion of conductivity type occurs only in the deformed portions of the specimen when processed in this manner the product of this process contains two n-p junctions 41 and 42. Thus, it is apparent that this technique of introducing acceptors in sufficient quantities to cause a conversion of conductivity type from n to p material by the permanent deformation of n-type semiconductive material at elevated temperatures can be employed to produce n-p junctions. Such junctions are prepared by maintaining a portion of the body cool enough so that the stresses applied to it are insufficient to deform it. Considered in its broader aspects, p-n junctions can be produced by the techniques of deformation by limiting the deformation to only a portion of the body so that a conversion occurs only in that portion. Similarly, since there is a certain minimum level of acceptors which must be introduced to convert an n-type semiconductor of a given resistivity (a given donor predominance) to p-type, it follows that junctions can be produced by deforming one portion of a body a sufficient amount to introduce an acceptor predominance therein, thereby converting that portion to p-type, while another adjacent portion is not deformed enough to introduce a sufficient density of acceptor centers to overcome the donor density originally present in the material. A net donor predominance exists in this latter material and, therefore, no conversion is effected.

By using the techniques described here, both graded and step junctions can be produced. Graded junctions are those which have a gradually decreasing predominance of acceptors on the p side and donors on the n side as the junction is approached. Graded junctions can be produced by a gradual change in the deformation induced. Step junctions have a steep gradient at the junctions with relatively high predominances of acceptors on the p side and donors on the n side close to the junction. A sharp demarcation in the degree of deformation between adjacent portions such as produced by maintaining a portion below the temperature permitting plastic flow while the adjacent portion is above that temperature will cause a step junction to result from stressing the body.

As seen in Fig. 4, a specimen deformed in compression exhibits a less regular strain marking than one deformed in tension. Due to the constraints imposed on the specimen surfaces by the compressing plates, deformation by continuous compression may not be imposed so uniformly over an extensive region of the specimen. These constraints may be avoided to some extent by permanently deforming the specimen only slightly, then removing the load to release the frictional forces between the specimen and the surfaces bearing against it, reloading the specimen to induce a further slight permanent deformation and repeating the cycle until the desired total permanent deformation has been attained. Since the instrumentation employed in compression is more amenable of control, lends itself to simpler forms, and permits the use of a closed system, it is advantageous to practice the conversion of conductivity type by the application of compressive stress.

Conversion of germanium and silicon of n-type con-

ductivity to p-type has been realized by compressive deformation. An n-type germanium body obtained from a single crystal having a resistivity of 5 ohm centimeters was deformed in the $\langle 001 \rangle$ direction about 5 percent in compression at 500° C. for 55 minutes and converted to 1.5 ohm centimeter p-type. This change corresponds to an introduction of about 10^{15} acceptor centers per cubic centimeter. Compression was performed between plates of tantalum in a dry helium atmosphere. A control specimen cut from the same crystal and similarly prepared was included simultaneously in the furnace and unstressed. No significant changes in resistivity were obtained in the control. The thermal cycle to which these specimens were subjected involved a uniform heating rate for ten minutes to bring them up to 480° C., a gradual increase to 500° C. over the next ten minutes interval, a dwell at 500° C. for 55 minutes, and a decrease to 100° C. over a 90 minute interval at an initially high rate of decrease.

The above specimens were one-quarter inch cubes having two faces approximately parallel to (100) planes and four faces approximately parallel to (110) planes. They were prepared by mechanical abrasion in the usual manner, by etching them in a solution consisting of 25 parts by weight nitric acid and 15 parts hydrofluoric acid, rinsing them in distilled water, immersing them in a 5 percent potassium cyanide solution for about 5 minutes, and rinsing them in distilled water which has been kept out of contact with copper bearing materials, e. g. de-ionized water. This technique of surface preparation is in accordance with that set forth in application Serial No. 334,972, filed February 3, 1953, by R. A. Logan and M. Sparks.

Another conversion of conductivity type was effected with an n-type germanium body obtained from a single crystal having a resistivity of 26 ohm centimeters which was compressed between tantalum plates for about 10 minutes at about 650° C. in an atmosphere of dry helium. The preparation of the specimen and a control specimen was performed in the manner set forth above. The stressed specimen was permanently deformed about 5 percent in the $\langle 001 \rangle$ direction and exhibited a p-type resistivity of about 3 ohm centimeters while the control specimen was substantially unchanged. These specimens were brought to the 650° C. temperature in 30 minutes, held at 650° C. for 10 minutes, cooled to 430° C. in 6 minutes, and cooled to 170° C. over the next 8 minute interval.

Small amounts of plastic deformation will convert high resistivity n-type material as evidenced by the following: an 8 ohm centimeter, n-type, single crystal, body of germanium was prepared by etching and immersion as set forth above and deformed in compression 1.5 percent in an $\langle 001 \rangle$ direction while heated at 500° C. for 15 minutes. The body converted to p-type and had a resistivity ranging from 14 to 22 ohm centimeters.

As set forth above it has been found that certain factors of the process appear to counteract each other. These factors, according to one view, are attributable to an introduction of acceptor centers by the deformation of the body coupled with a healing of crystal structure vacancies or other defects. This healing occurs as a function of time and temperature to effectively introduce donor centers by way of the elimination of acceptor centers. Thus, the longer a specimen is held at an elevated temperature and the higher the temperature the greater the healing. This suggests that limits of temperature and time at temperature apply to the process and further indicates that the specimens should be deformed as rapidly and at as low a temperature as is possible without fracturing them. Examples which indicate the effect of the counteracting action of simultaneously introducing acceptor and donor centers follow:

N-type germanium bodies obtained from a single crystal of 8.3 ohm centimeters resistivity or a conductivity of

about 0.12 mho centimeter⁻¹ were prepared as set forth above in the case of the second compressed specimen and subjected to an 800° C. heating cycle for about 5 minutes. This heating cycle was effected by raising the temperature to 800° C. over a 15 minute interval, holding the specimens at 800° C. for 5 minutes, cooling them to 500° C. over a 30 minute interval and to room temperature from 500° C. in 50 minutes. One specimen was compressed in an <001> direction so that it was permanently deformed in the direction of compression 22 percent while the other specimen was unstressed and employed as a control. The deformed specimen converted to p-type and had a resistivity of about 9 ohm centimeters or a conductivity of about 0.11 mho centimeter⁻¹ corresponding to the introduction of 6×10^{14} acceptor centers due to deformation. The undeformed specimen remained n-type and had a resistivity of about 18 ohm centimeters.

A pair of specimens having characteristics comparable with those above indicate that the above deformation treatment occurred near the crossover point for the introduction of acceptor centers by deformation, i. e. that limit beyond which the heating and deforming techniques of this process cause a decrease in the number of acceptor centers normally introduced by the heating cycle alone. These specimens were obtained from a 5 ohm centimeter single crystal of n-type germanium. The specimens were brought to a temperature of 850° C. in 16 minutes, held at 850° C. for 15 minutes, cooled to 620° C. in 3 minutes, and cooled from 620° C. to 200° C. in 20 minutes. The stressed specimen was permanently deformed 25 percent along the <001> direction (the direction in which the compressive force was applied) and converted to about 17 ohm centimeter p-type. This indicates that about 5×10^{14} acceptor centers were introduced during the heating cycle and deformation. The unstressed control specimen, however, converted even more p-type to about 1 ohm centimeter material, thus indicating an introduction of about 3.6×10^{15} calculated acceptor centers due to thermal effects alone.

From a comparison of the results of the two immediately preceding examples of comparable material it appears that a crossover point occurs for the number of acceptor centers and donor centers introduced in n-type germanium material of 5 to 8 ohm centimeters resistivity which is permanently deformed about 25 percent at some heating cycle between a 5 minute treatment at 800° C. and a 15 minute treatment at 850° C. The 5 minute 800° C. treatment caused an introduction of 1.1×10^{14} calculated acceptor centers in the undeformed specimen and the 22 percent deformation at that temperature introduced 6×10^{14} calculated acceptor centers. Clearly stressing the sample at this temperature introduces acceptor centers in addition to those caused by the heating cycle alone. On the other hand at 850° C. there was actually a counteracting of the usual thermal introduction of acceptors by deforming the material and fewer acceptor centers were introduced in the deformed specimen than in the undeformed specimen.

Further verification of the existence of a limit on this process as a technique for introducing acceptor centers into germanium due to the relaxation at a temperature slightly below 850° C. has been obtained. A 5.3 ohm centimeter single crystal, germanium sample prepared as above and plastically deformed in compression 8.5 percent in the <001> direction while heated to 850° C. for 15 minutes converted to 23.5 ohm centimeter p-type while a similar control specimen converted to 1.4 ohm centimeter p-type. Again it is seen that more acceptors were introduced into the undeformed specimen than into the deformed specimen.

While some variation in the heating cycle at which relaxation occurs in the crystal at a more rapid rate than acceptor centers are introduced may occur with variations in the resistivity of the material and variations in

the length of the cycle, it appears that the maximum temperature for all germanium is about 850° C. or 92 percent of the melting temperature on the absolute scale. A similar limit percentagewise is placed on silicon processed according to this invention.

Silicon specimens have been deformed in compression to introduce acceptor centers therein. N-type silicon of 6 ohm centimeters resistivity has been compressed in an <001> direction 2.5 percent at 725° C. and 18 percent at 850° C. These specimens were cut from single crystals, abraded, and polished in an etchant composed of 20 cubic centimeters of nitric acid (1.42 specific gravity) and 5 cubic centimeters of hydrofluoric acid (48 percent), rinsed in double distilled water, and dried. Their firing cycles occurred in an atmosphere of helium and involved raising them to temperature over a 30 minute interval, holding them at temperature for 18 minutes while they were stressed, and cooling them to ambient in 30 minutes. In the first instance the material remained n-type but had a resistivity of 150 ohm centimeters. A conversion to p-type material was realized by the greater deformation, this material exhibited a resistivity of about 50 ohm centimeters. Calculations indicated that about 10^{15} acceptor centers per cubic centimeter were introduced by the above deformation. Unstressed control specimens were included within the furnace in both of these deformation runs. No significant changes in resistivity were obtained in the controls.

Apparatus suitable for the compressive deformation of semiconductors is shown in Fig. 6. It comprises a furnace tube of fused silica 60 surrounded by a ceramic tube 61 on which is wound a resistance heater 62. The lower end of the furnace tube is closed with a head 63 provided with passages 64 for cooling fluid which is supplied through tube 65 and exhausted through tube 66. A seal 67 which may be of wax or a lead gasket is positioned between head 63 and the furnace tube 60 so that the furnace atmosphere may be entirely independent of the external atmosphere. The opposite end of the furnace tube 60 is sealed to a fluid cooled ring 68 by a seal 69. Cooling coils 71 surround ring 68 and are supplied with coolant by tube 72. A silphon bellows 73 is secured in gas tight relationship as by brazing to the upper portion of ring 68 and is connected by a gas tight joint to a cap 74. Gas of a desired composition is supplied to the closed furnace through tube 75 in head 63 and exhausted through tube 76 in ring 68.

A specimen 77 to be compressed is mounted in the furnace between cleaned plates 78 of tantalum on each side of which are located high strength ceramic columns 79 and 80 of a material such as mullite. A centering sleeve 81 of stainless steel surrounds the assembly and engages projections on the periphery of a tantalum centering disc 82 containing a square, central aperture having upwardly flanged edges 83 for positioning the specimen to be stressed.

In operation column 79 rests on the head 63 and provides a base for the fixed plate 78. Column 80 fits into and is engaged by the walls of seat 85 in cap 74 which is positioned under the platen 86 of a press (not shown). When a compressive force is applied to the cap 74 by the press, it is transmitted to the specimen through column 80 and upper plate 78. The furnace wall section provided by silphon bellows 73 is sufficiently flexible to permit the longitudinal movement of cap 74 without imposing any substantial amount of force on the remainder of the furnace structure.

The specimen is deformed by mounting it in the furnace as shown in Fig. 6, sealing the furnace and flushing it with a suitable gas which will have no detrimental effect on the specimen, for example dry, chemically pure helium. Heat is then applied to the furnace by means of a suitable power supply connected through control and monitoring means (not shown) to heater 62 and the furnace is brought up to temperature at the desired rate. It may be noted here that the temperature of the specimen can be monitored

by positioning the hot junction of a chromel-alumel thermocouple in a protective quartz tube in close proximity to the sample much in the manner disclosed in the apparatus of Fig. 5. When the specimen reaches temperature, the load is gradually applied. It has been observed, particularly at the lower temperatures, that the immediate application of the total load causes the specimen to fracture, presumably due in part to the uneven stressing of the material resulting from slight irregularities in the mating surfaces, and further to the need of an incubation period for the nucleation or reorientation of the localized structural configurations permitting flow, i. e. dislocations. However, a gradually increased load can be applied at temperatures of about 500° C. for germanium and 725° C. for silicon without any cracking of the material since the irregularities are deformed and the stresses distributed by the plastic flow of the material in those regions subjected to the greatest stresses. Thus when the full load is applied the specimen is uniformly stressed.

Again it is to be noted that while an incubation period during loading at the lower deformation temperatures renders it advantageous to apply the deforming load gradually, there are other factors which are introduced at rates which are functions of time and temperature, including thermally introduced acceptors and lattice defect healing which become quite pronounced at higher temperatures (above about 650° C. for germanium and about 900° C. for silicon).

Recapitulating, in accordance with this invention, acceptor centers can be introduced into germanium and silicon by deforming the material at temperatures in excess of about 60 percent of their melting temperatures on an absolute scale (about 500° C. for germanium and about 725° C. for silicon). These centers can be introduced in such densities as to overcompensate the donors in n-type material and convert that material to p-type when it is initially of a resistivity greater than 1 ohm centimeter for germanium and about 5 ohm centimeters for silicon. The number of acceptor centers introduced at a particular deformation temperature is a function of the amount of deformation in the material. The acceptor centers introduced by deformation are unlike chemically introduced acceptor centers in that they are not removed from the material by annealing processes involving long soaks at temperatures of about 500° C. The semi-conductive materials exhibit an upper limit for the heating cycle which can be employed in the deformation technique of introducing acceptor centers such that deformation with heat cycles above that limit causes a reduction in the number of introduced acceptor centers. This upper limit of temperature for heat treating intervals of about 15 minutes is about 850° C. for germanium. Thus the most advantageous results of the process are realized by operating at a deformation temperature of between about 500° C. and about 650° C. with an upper limit of about 850° C. for germanium and between about 725° C. and about 900° C. with an upper limit of about 1260° C. for silicon. Time for deformation within these ranges should be kept to a minimum consistent with processing the material without cracking it either by excessive stresses or thermal shocks, i. e. the material should be maintained at temperature the minimum interval sufficient to realize the desired degree of plastic flow and should be brought to and lowered from temperature as rapidly as possible. While acceptor centers can be introduced by imposing any form of permanent deformation on silicon and germanium including tensional, torsional, compressive, shearing, and com-

binations of the above deforming stresses, e. g., bending, from the standpoint of instrumentation compressive deformation is most convenient.

It is to be noted that the minority charge carrier lifetimes in permanently deformed material may be materially reduced from their normal level. This reduction in lifetime renders this material of such a nature that devices constructed of it have low reverse recovery times and are therefore particularly good high frequency switches. It should also be noted in this regard that the number of acceptor centers introduced in deformed material has been calculated from the initial charge carrier lifetime and mobility and in view of the changes therein are not absolutely correct, but rather indicate their magnitude.

It is to be understood that the above-described techniques are illustrative of the application of the principles of the invention. Numerous other arrangements may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of producing a p-n junction in a solid body of a semiconductive material selected from the group consisting of germanium and silicon, said body manifesting n-type conductivity and having a resistivity of at least one ohm-centimeter, comprising heating at least a portion of the said body to a temperature of above 60 percent of the melting temperature of the said semiconductive material on an absolute temperature scale, applying stress to the said body so as to strain only the said portion beyond its elastic limit whereby the strained portion is converted to p-type so that a p-n junction results between the said strained portion and the remainder of the body and cooling the said body.

2. The method of claim 1 in which the temperature to which the said portion is heated is within the range limited by 92 percent of the melting temperature of the said semiconductive material on an absolute temperature scale.

3. The method of claim 2 in which the semiconductive material is germanium and in which the said temperature range is from about 500° C. to about 850° C. and in which the said body is cooled to at least 100° C. immediately following imposition of the said stress.

4. The method of claim 2 in which the semiconductive material is silicon, in which the said body has a resistivity of at least 5 ohm-centimeters and in which the said temperature range is from 725° C. to 900° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,402,661	Ohl	June 25, 1946
2,449,484	Jaffe	Sept. 14, 1948
2,530,110	Woodyard	Nov. 14, 1950
2,563,503	Wallace	Aug. 7, 1951
2,629,800	Pearson	Feb. 24, 1953
2,725,318	Gallagher	Nov. 29, 1955
2,732,519	Freedman	Jan. 24, 1956

OTHER REFERENCES

Barrett: Structure of Metals, published by McGraw-Hill Book Co., New York, N. Y., 1943, pp. 260 and 261.
Doan: Principles of Physical Metallurgy, published by McGraw-Hill Book Co., New York, N. Y., 1953, 3rd ed., pp. 92 and 93.

Chalmers: Progress in Metal Physics, 4. Published by Interscience Publishers, New York, N. Y., 1953, pages 263, 237 and 262.