Aug. 18, 1964 H. LETAW, JR., ETAL 3,145,328

METHODS OF PREVENTING CHANNEL FORMATION ON SEMICONDUCTIVE BODIES

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FIG. 1 CASE I

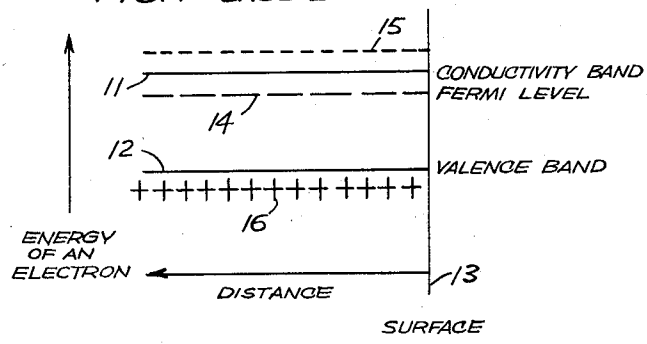


FIG. 4 CASE I

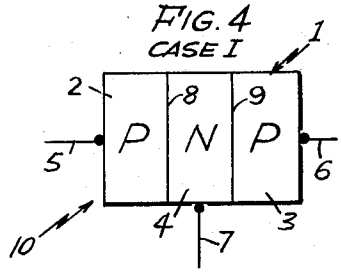


FIG. 2 CASE II

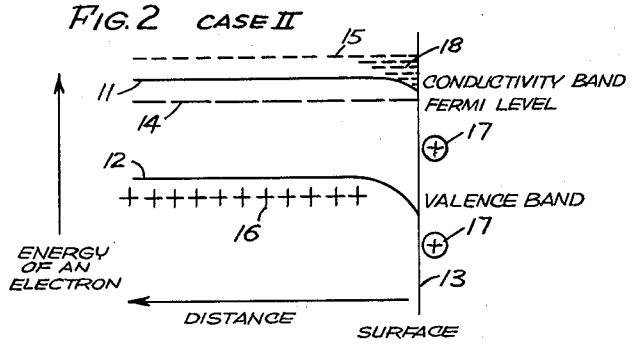


FIG. 5 CASE II

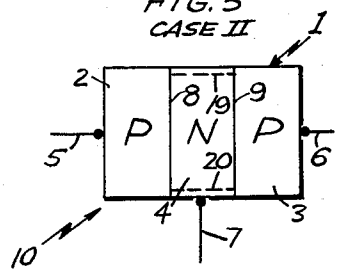


FIG. 3 CASE III

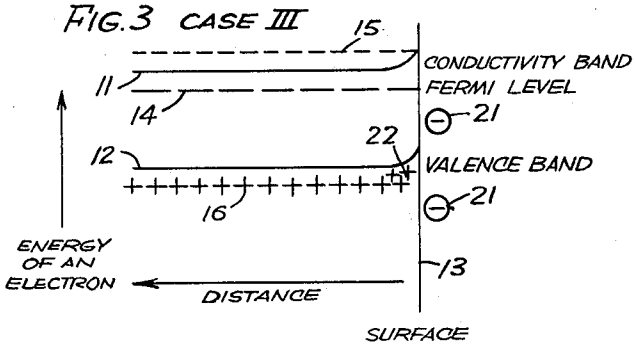
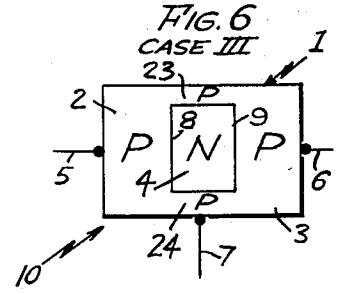


FIG. 6 CASE III



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METHODS OF PREVENTING CHANNEL FORMATION ON SEMICONDUCTIVE BODIES

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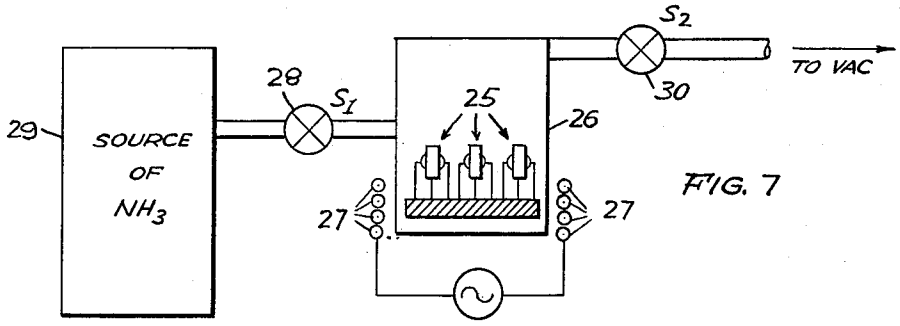


FIG. 7

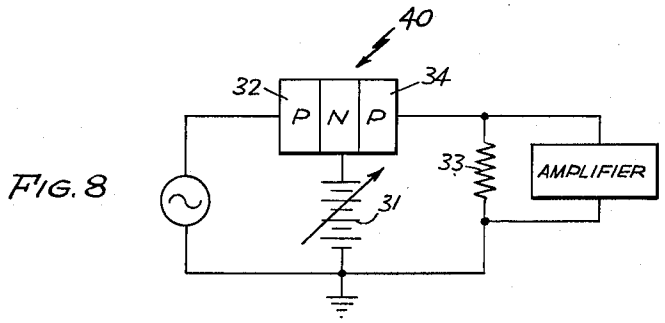


FIG. 8

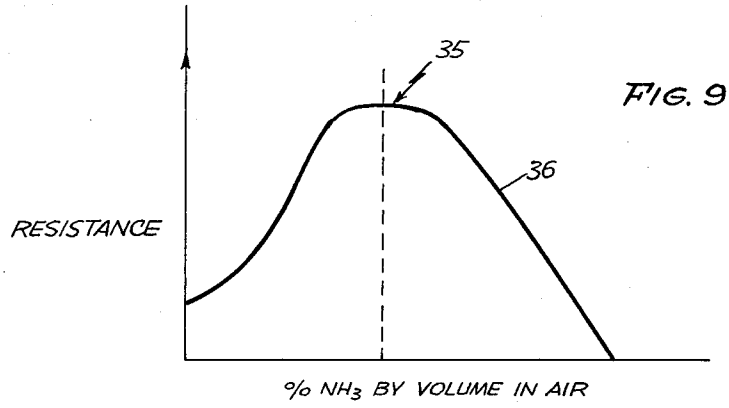


FIG. 9

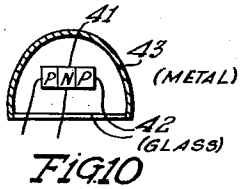


FIG. 10

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METHODS OF PREVENTING CHANNEL FORMATION ON SEMICONDUCTIVE BODIES

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5 Claims. (Cl. 317—234)

This invention relates generally to the improvement of the electrical characteristics of semiconductive material for use in the manufacture of semiconductive devices, and more particularly to a novel method of preventing and inhibiting the formation of undesirable short-circuiting channels on or closely adjacent to the surface of the semiconductive material.

The electrical characteristics of semiconductive material, such as silicon and germanium, are largely determined by small traces of impurities or slight mechanical defects which are present on the surface or within the bodies of the materials. A pure crystal of silicon or germanium is made up of a cubic lattice in which each atom has four valence electrons, all of which are bound in the lattice. The presence of what is termed "significant" impurities disrupts the lattice structure. The impurities are of two different types; those designated "donor" impurities which, upon replacing an atom in a crystal lattice, supply more than the four needed electrons, and those designated "acceptor" impurities which supply less than the needed four electrons. The former type supplies unbonded electrons which serve as negative mobile charge carriers and the latter, electron deficiencies or "holes" which serve as positive mobile charge carriers. A semiconducting material in which conduction by "holes" normally occurs, that is, where the majority current carriers are "holes," is identified as P type, whereas the type in which the principal conduction occurs by electrons, i.e., the majority current carriers are electrons, is identified as N type.

Semiconductive devices are now known which comprise a body of semiconductive material having adjacent regions or zones of N-type and P-type material with the interface between any N-type and P-type region constituting a P-N rectifying junction. The various zones are provided with appropriate conducting electrodes connected thereto, and the finished unit may then be used to perform signal amplifying or other electrical translating functions.

Devices of the class described have been heretofore subject to the disadvantageous feature that channels of material of opposite electrical conductivity-type to that of the bulk of the semiconductor are often formed on or closely adjacent to the surface of the semiconductive material which permit a high density of minority carriers to concentrate in a region near the surface. These channels constitute a conducting path which is, in effect, a low impedance electrical circuit between the adjacent N and P conductivity-type regions and leads to shorting between the regions. This effect may or may not totally destroy the usefulness of devices made of a semiconductive material on the surface of which the channels have formed, but in most cases, the channels act to seriously impair the performance of the devices. Several methods of avoiding channels have been proposed in the past. One of these (and the most difficult to apply) is to obtain a clean surface on the semiconductive material and to thereafter maintain the semiconductive material in a vacuum. This method, unfortunately, has proven to be too impractical to utilize in large scale production. Another method has been to clean the surface of the semiconductive material as much as possible and

then to protect it by painting with a suitable plastic material which may or may not contain intentionally-added impurities. However, none of the proposed prior art methods of channel avoidance has proven to be completely satisfactory.

Accordingly, the present invention is directed toward a novel manner of treating the surface of the semiconductive material which effectively overcomes the formation of channels thereon and, consequently, leads to the production of more useful devices. It has been found that the channels are caused by the production of an electronic charge on the surface of the semiconductive material which effectively converts the surface region to an electrical conductivity type which is opposite to that of the conductivity type of the bulk of the semiconductive material. The present inventive concept involves a novel method of treating the semiconductive body so as to neutralize this electronic charge whereby, in effect, the surface material is reconverted to the same electrical conductivity-type as the bulk of the semiconductive material and the undesired channels are eliminated.

The invention will be better understood as the following description proceeds taken in conjunction with the accompanying drawings wherein:

FIG. 1 is an energy level diagram useful in illustrating electronic conditions existing at the surface of an N-type body of semiconductive material relative to electronic conditions in the bulk material;

FIG. 2 is an energy level diagram similar to that shown in FIG. 1 illustrating the case where the surface of the N-type semiconductive material is considerably more N-type than the bulk of the material;

FIG. 3 is an energy level diagram similar to those shown in FIGS. 1 and 2, but illustrating the case where the surface is P-type and the bulk material is N-type;

FIG. 4 is a schematic representation of a PNP transistor wherein the N-type base region corresponds to conditions illustrated in FIG. 1;

FIG. 5 is a schematic representation of the transistor shown in FIG. 4 when the surface of the N-type base region has been changed to correspond to conditions illustrated in FIG. 2;

FIG. 6 is a schematic representation of the transistor shown in FIG. 4 when a P-type channel has formed on the surface of the N-type base region, and corresponds to conditions illustrated in FIG. 3;

FIG. 7 is a diagrammatic showing of an exemplary way of carrying out the method of the present invention;

FIG. 8 is a schematic diagram of a circuit useful in evaluating the effect of the channel-preventing method of the present invention;

FIG. 9 is a graph showing the resistance of the region of the semiconductive material to which the channel preventing substance has been applied plotted against the percentage of substance used, as determined by utilizing the test circuit of FIG. 8; and

FIG. 10 is a diagrammatic showing of a completed transistor having a housing containing a Lewis-base in a gaseous state.

Referring now to the drawings, and more particularly to FIGS. 1 through 6, there is shown generally at 10 a semiconductive device comprising a body of semiconductive material 1 having a plurality of spaced P-type zones 2 and 3, and an intermediate N-type zone 4. The N and P type zones may be prepared in any way well known in the art, as by properly doping a growing crystal of the semiconductive material with suitable impurity materials, or by alloying dots of impurity material into opposite sides of a sliced chip of semiconductive material. The P-type regions 2 and 3 may then be respectively provided with electrical connections 5 and 6, and

the N-type region provided with an electrical connection 7. Such a device is designated in the art as a PNP transistor, with the regions 2 and 3 being termed, respectively, the emitter region and collector region, while the intermediate region 4 is termed the base region. The interfaces 8 and 9 between the N-type and the P-type zones constitute P-N junctions.

As has been previously described, such devices are frequently subject to the formation of channels on the surface of the body 1, which channels extend across the PN junctions 8 and 9 thereby creating conducting paths between the regions 2 and 4 or 3 and 4, which impair the usefulness of the device 10 for its intended purpose. This effect will be further understood by reference to FIG. 1 which shows the energy level diagram applicable to an N-type material such as the base region 4 of the transistor shown in FIG. 4. The long dashed line 14 represents the Fermi level, while the dotted line 15 represents free electrons associated with the bottom of the conduction band 11. Similarly, the line of small plus signs 16 represents holes associated with the top of the valence band 12. In this instance, the conductivity band 11 and the valence band 12 are both perpendicular to the line 13 representing the surface of the semiconductive body 1, thereby indicating an electronic charge equilibrium condition at the surface of the body 1 and, conseqently, no channel formation.

When an effective positive charge is somehow formed on the surface of the semiconductive body 1, as indicated by the encircled plus signs 17 adjacent the surface line 13 of FIG. 2, the lines 11 and 12, respectively, representing the conductivity band and the valence band are caused to turn downwardly and result in a greater concentration of free electrons being available at the surface of the body 1, as represented by the massed electrons 18. Consequently, N-type region 4 becomes more strongly N-type near the surface thereof, which effect is pictorially shown by the dotted lines 19 and 20 across the region 4 of the transistor of FIG. 5. Although the regions between the dotted lines 19 and 20 and the adjacent outside edges of the body 1 now technically constitute channels, they are not of the type detrimental to transistor operation since they are still composed of N-type material. However, when a negative charge is applied to the surface of semiconductive body 1, as indicated by the encircled minus signs 21 adjacent the surface line 13 of FIG. 3, the lines 11 and 12, respectively, representing the conductivity band and the valence band are caused to turn upwardly, resulting in a greater concentration of holes being available at the surface of the body 1, as represented by the massed holes 22. This effect arises from the repulsion of electrons remaining in the semiconductor by the field of the negatively-charged surface layer, and results in a greater concentration of holes being available at the surface of body 1. Consequently, a portion of the N-type base region 4 near the surface of the body 1 is converted to P-type material, and forms the P-type channels 23 and 24 shown in FIG. 6. As can be seen, the channels 23 and 24 extend completely across the junctions 8 and 9, thereby effectively short-circuiting the junctions and destroying the usefulness of the device as a transistor.

In accordance with the present invention, the formation of P-type channels such as 23 and 24 may be inhibited or prevented by subjecting the surface of the N-type base region 4 to treatment by a quantity of donor-type matter. The term "donor-type matter" as used in this specification is intended to include any matter which, when chemically adsorbed on the surface of the body 1, will act as a donor of electrons to the surface atoms of the body, and thus create an N-type surface region. It has been found that any Lewis base (or donor-type vapor or gas) represent examples of donor-type matter which may be successfully used to prevent the formation of P-type channels on N-type semiconductive material, as long as they do not contribute to a second conduction phenomenon known as "pseudo-ionic conduction," the effects of which will be more fully explained below.

FIG. 7 shows one manner of accomplishing channel prevention in accordance with the principles of the present invention. As shown, the process is applied to a plurality of fused alloy-type PNP transistors 25, the surfaces of which have been previously cleaned as by etching, and which are contained in a vacuum bake-out chamber 26 heated by the coils 27 to a conventional bake-out temperature of approximately 150 to 200° C. as is well-known in the art. After the baking process is completed, the valve 28 may be opened to admit a quantity of a donor-type gas as, for example, ammonia which may be entrained at normal or reduced pressure in a dry inert gas, such as nitrogen, or other ambient gas which has little or no effect on the electrical characteristics of the semiconductive body, to the chamber 26 from a suitable source 29. After subjecting the transistors 25 to the gaseous ammonia atmosphere for a period of a few minutes, valve 30 may be opened to allow the ammonia to escape from the chamber 26, and the transistors 25 may be removed therefrom for subsequent packaging into a finished unit. It should be noted that the amount of donor-type material adsorbed on the transistors 25 is critical in that the final adherence of too great a concentration tends to lead to the inducement of excess surface leakage current due to the "pseudo-ionic conduction" phenomenon mentioned above, with the result that a more serious shorting path than the original channel is often created. In consonance with this, any amount of donor-type material may be used in the initial application step as long as the excess is subsequently removed, as for example by baking or pumping, in order to achieve and maintain the final critical percentages. Accordingly, it has been determined that, in the case of gaseous ammonia, the concentration of ammonia in the atmosphere of the chamber 26 should preferably range from about .05 percent to about .5 percent by volume in the ambient atmosphere in order to prevent the occurrence of this deleterious effect. When other donor-type gases are used, the critical percentage concentrations used may vary from the .05 percent to .5 percent range of ammonia necesary to produce optimum resistance conditions on the surface of the semiconductive body. In order to determine whether or not the correct percentage of donor-type material is being utilized, the semiconductor under treatment may be tested in the circuit configuration shown in FIG. 8, wherein the schematically-illustrated PNP transistor 40 is provided with a bias battery 31 connected to the N-type base region, a source of 1,000 cycle alternating current connected to the P-type emitter region 32, and a resistor 33 connected to the P-type collector region 34. When the amplified voltage drop across the resistor 33 is in a minimum range optimum resistance conditions exist on the surface of the transistor 40 as indicated by the peak region 35 of the curve 36 shown in FIG. 9. If desired, the containers in which the transistors 25 are housed when the fabrication process is finally completed may contain an atmosphere of donor-type material not exceeding the percentages disclosed in order to permanently protect the finished units against subsequent channel formation. FIG. 10 shows a PNP transistor 41 encapsulated, having a glass base 42 to which is sealed a housing 43 which contains a Lewis base atmosphere to prevent channeling on the surface of the transistor 41, as described in conjunction with FIGS. 1 to 6.

Although the present inventive concept has thus far been described with respect to the prevention of P-type channels on N-type semiconductive material, it should be understood that N-type channels may be inhibited or prevented from occuring on the surface of P-type semiconductive material by subjecting the surface of the P-type material to treatment by a quantity of acceptor-type matter. As used in this specification, the term "acceptor-type matter" is intended to include any matter which,

when chemically absorbed on the surface of a P-type body, will act as an acceptor of electrons from the surface atoms of the P-type body, and thus create or maintain a P-type surface region. It has been found that any Lewis acid (or acceptor-type vapor or gas) represent examples of acceptor-type matter which may be successfully used to prevent or inhibit the formation of N-type channels on P-type semiconductive material. For instance, boron trifluoride and boron trichloride have both been successfully utilized to prevent channel formation on NPN transistors in a manner similar to that described above with respect to the PNP transistors **25** shown in FIG. 7 wherein either gaseous boron trifluoride or boron trichloride was provided in chamber **29** instead of ammonia, and transistors **25** were NPN instead of PNP.

Although there have been described what are considered to be preferred embodiments of the present invention, various adaptations and modifications thereof may be made without departing from the spirit and scope of the present invention, as defined in the appended claims.

What is claimed is:

1. The method of producing a semiconductive device comprising preventing P-type channel formation on an N-type semiconductive body by subjecting the exposed surface of the body to a gaseous atmosphere of substantially a donor-type impurity, said impurity adsorbing on the surface of said body at a temperature below that which will cause any substantial diffusion of said impurity material into said body.

2. The method of producing a semiconductive device comprising preventing P-type channel formation on an N-type semiconductive body by causing a donor-type impurity to adsorb on the surface of said body at a temperature below that which will cause any substantial diffusion of said impurity material into said body, said material comprising ammonia ranging from about .05 percent to about .5 percent by volume in the ambient atmosphere.

3. A semiconductive device comprising a body of semiconductive material having a plurality of regions of P-type electrical conductivity material and an intermediate region of an N-type electrical conductivity material, a housing enclosing said body, and a quantity of a donor-type impurity in the gaseous state contained in said housing and adapted to produce the same electrical conductivity-type material at the surface of said body as exists in said intermediate region.

4. A method of producing a semiconductive device comprising neutralizing stray positive electronic charges present on the surface of a semiconductive body by subjecting the surface of said body to a quantity of donor-type vapor at a temperature below that which will result in any substantial solid-state diffusion of said material into said body to produce on the surface a negative electronic charge.

5. The method of producing a semiconductive device comprising preventing and correcting N-type channel formation on a semiconductive body containing P-type electrical conductivity-determining impurity material, said method comprising subjecting the surface of said body to a quantity of matter selected from a group consisting of boron trifluoride and boron trichloride at a temperature below that which will result in any substantial solid-state diffusion of said matter into said body.

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