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PATENT SPECIFICATION 978,561

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Improvements relating to Transistors.

We, TEXAS INSTRUMENTS INCORPORATED, of 13500 N. Central Expressway, Dallas, Texas, United States of America, formerly of 6000 Lemmon Avenue, Dallas, Texas, United States of America, a Corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to transistors.

Semiconductor materials have come into prominence recently because of their usefulness in making such devices as transistors, and certain elements of Group IV*a* of the periodic table of elements, i.e., carbon, silicon, germanium and tin, have in common the characteristics requisite for semiconductor materials. (As used herein, the periodic table of elements shall mean that table according to Mendelejeff as now generally portrayed.) However, because of the difficulty of synthetic production of the diamond form of carbon and the instability of the diamond lattice in tin, the semiconductor materials first used and now most commonly used in the aforesaid devices are germanium and silicon.

Nevertheless, because of certain inherent limitations of germanium and silicon as semiconductor materials and because of the difficulties of producing and maintaining the diamond lattice structure in tin and carbon, experimenters have been diligently searching for other and better semiconductor materials. The so-called semiconductor compound materials which are comprised of an element from Group III*a* and an element from Group V*a* of the periodic table appear superior to the Group IV*a* semiconductors in many of their characteristics.

Among the properties affecting the usefulness of a material as a semiconductor are its forbidden energy gap, its minority carrier mobility and lifetime, and its crystal lattice structure.

Semiconductor materials are characterized by discrete electron energy levels or bands. The electrons forming the bonds of saturable valence force acting between the immediately adjacent atoms of the cubic lattice structure do not contribute to electrical conductivity, and are said to exist in the valence band or energy level. The electrons possessing a higher energy level are said to reside in the conduction band. No electrons can possess energy at a level intermediate these two energy levels and, therefore, the gap between the valence band and the conduction band is known as the forbidden energy band or gap. This forbidden energy band varies substantially among the various semiconductor materials. For example, in germanium the forbidden energy band is about 0.75 electron volts in width. Silicon has a forbidden energy band approximately 1.1 electron volts wide. The width of the forbidden energy band of a semiconductor material is one of the factors affecting the range of temperatures over which devices made from that material are operative. Heating the semiconductor material produces thermal excitation of the electrons and will cause electrons in the valance band to obtain sufficient energy to come into the conduction band. Thus, each material ionizes sufficiently at some temperature that its semiconducting properties are destroyed and it becomes essentially a conductor. For this reason, germanium is useful only up to about

85° C., and silicon only to approximately 200° C.

The electron or "carrier" mobility in a semi-conductor material is a factor greatly affecting the frequency response of any devices made from that material and the physical parameters, such as base width, required in such devices to make them operable. As the carrier mobility increases, the frequency response of the semiconductor device also increases. Thus, germanium with an electron mobility of approximately three times that of silicon, provides a much greater frequency response in devices made from it than is obtainable in comparable devices made from silicon. Hence, although semiconductor devices of silicon may operate at higher temperatures than those of germanium, the frequency response of the silicon devices is somewhat limited as compared with that of germanium.

The lifetime of minority carriers in a semiconductor material, which is a function of the number of carriers available and their mobility within the crystal, is a factor also affecting the electrical parameters of any device made from the material. In certain types of devices, the lifetime is desired as low as possible; in others, a higher lifetime is required,

Because extremely pure semiconductor materials have very few electrons in the conduction band (within their usable temperature range) and are essentially insulators, carriers in the form of either electrons as negative carriers or holes, as positive carriers, with energies in or near the conduction band must be provided in the semiconductor material for the fabrication of workable devices. These additional carriers are provided by minute amounts of impurities in the material. The type and number of carriers provided is determined by the particular impurity and the amount added. In germanium and silicon, N-type or donor impurities—those producing excess electron carriers—are selected from the elements of Group V*a* of the periodic table, usually phosphorus, arsenic and antimony, and P-type or acceptor impurities—those producing hole carriers—are selected from the elements of Group III*a* of the periodic table, usually boron, aluminium, gallium and indium. When an atom of a Group V*a* impurity, which has five electrons in its outer shell, is substituted for an atom of germanium or silicon, which have four electrons in their outer shells, four of the electrons in the impurity atoms enter into the bonds with adjacent germanium or silicon atoms, leaving an extra carrier electron. In the same manner, substitution of an atom of a Group III*a* impurity (three valence electrons) for a germanium or silicon atom leaves an electron deficiency or hole.

Because of the possibility of the wider range of selection and different combinations of the various characteristics mentioned above, the III*a*-V*a* compounds offer many advantages over germanium and silicon as semiconductors. For example, various combinations of Group III*a* and Group V*a* elements offer energy gaps ranging from 0.45 electron volts to 1.6 electron volts and carrier mobilities up to twenty times that of silicon.

Of the Group III*a*-V*a* semiconduuctor compounds, gallium arsenide apparently has the greatest potential as a semiconductor material. Its forbidden energy band is near that of silicon (1.35 electron volts) and its carrier mobility is very nearly that of germanium. Thus, gallium arsenide semiconductor devices will have very good high frequency response, and will be operative up to temperatures of about 400° C.

Despite the inherent advantages of gallium arsenide, certain difficulties have prevented its use in transistors to any important degree, as yet. Among these are the difficulties of producing a material of the requisite purity, and the difficulties of adding required amounts of significant impurities or "dopes" to the material to produce the P- and N-type regions required in transistors. The significant P-type impurities (Group III*a* elements, boron, aluminium, gallium and indium) and the significant N-type impurities (Group V*a* elements, phosphorus, arsenic, and antimony) used with the Group IV*a* semiconductor materials of silicon and germanium are relatively easy to control in the various growing, allowing and diffusion processes used in the fabrication of transistors. Although the P-type significant impurities (acceptors) of Group II*a* of the periodic table for the III*a*-V*a* compound semiconductor materials have proved manageable, the N-type impurities (donors) of Group VI*a* of the periodic table have proved quite difficult to handle because of their high vapour pressures. This has been especially true in connection with gallium arsenide wherein one of the elements of the compound is much more volatile than the other and the compound tends to dissociate at the temperatures required for diffusion or alloying of Group VI*a* elements. For this reason, there have been intensive investigations directed toward finding other materials suitable at N-type dopes for gallium arsenide. Because the properties of elements of Group IV make them more manageable, investigations were launched in hopes that these elements might prove suitable as dopes,, either N- or P-type, depending on which element of the III*a*-V*a* compound had some of its atoms replaced by atoms of the Group IV*a* element in the crystal. However, reports from these investigations

indicate that the Group IV*a* elements of silicon, germanium and tin substitute in gallium arsenide in "nearest neighbour pairs", i.e., two atoms of the Group IV*a* element replace one atom of the Group III*a* element and an adjacent atom of the Group V*a* element (its nearest neighbour), with a result that the material remains electrically neutral.

Contrary to the teaching of the prior art, it has been discovered that certain Group IV*a* elements will enter gallium arsenide as N-type impurities, and particularly, that tin will produce excellent results as a donor impurity in gallium arsenide. The unexpected properties of N-type gallium arsenide obtained from doping with tin make this material especially suitable for the fabrication of transistors.

The present invention is a transistor comprising a body of gallium arsenide having therein a region of P-type conductivity, and having alloyed to at least a portion of said region of P-type conductivity a body comprised of tin or principally of tin.

The present invention will now be described by way of example, with reference to the accompanying drawing, in which: —

Figs. 1*a* to 1*e* are schematic representations of the crystal lattice structure of gallium arsenide, showing the action of donor and acceptor impurities;

Figs. 2*a* to 2*c* illustrate the steps in the fabrication of a gallium arsenide diffused base transistor according to the present invention; and

Fig. 3 illustrates a gallium arsenide alloy transistor element made according to the present invention.

Turning now to Fig. 1*a*, there is illustrated schematically the crystal lattice structure of the III*a*-V*a* semiconductor compound, gallium arsenide. It is to be remembered that this is only a two dimensional expression of a three-dimensional structure. The crystal lattice or a semiconductor compound is quite similar to the diamond crystal lattice of a Group IV*a* semiconductor wherein double bonds are formed between each atom of the material with each atom contributing four electrons with each adjacent atom. In the semiconductor compound crystal, which is of the zinc blende structure, double bonds are also formed between each atom. However, this crystal lattice differs in that each atom of the Group III*a* element, gallium in the Figure, contributes only three electrons as indicated by the light lines 10 and each atom of the Group V*a* element contributes five electrons as indicated by the heavier lines 11. As illustrated in Fig. 1*b*, the compound may be caused to have P-type conductivity (excess holes) by substituting atoms of some Group II*a* elements 12, such zinc, for some gallium atoms. Since zinc has only two valence electrons, its inclusion in the lattice produces an electron deficiency (hole 13). An N-type conductivity structure will be produced if Group VI*a* element atoms 14, such as selenium, are substituted for some of the arsenic atoms, as illustrated in Figure 1*c*. Since Group VI*a* elements have six valence electrons, as compared to five in arsenic, one electron 15, in excess of the number required to produce all of the double bonds, is present in the lattice. Materials producing N-type conductivity are called donors, and those producing P-type conductivity are called acceptors.

It might seem logical to substitute Group IV*a* atoms (four valence electrons) in the lattice to act either as a donor if it replaced the gallium atom—three valence electrons—or as an acceptor if it replaced an arsenic atom—five valence electrons. Indeed, this type of doping was investigated. Prior art reports, however, state that the Group IV*a* elements of tin, germanium, and silicon act neither as donors nor acceptors in III*a*-V*a* compounds and explain that these Group IV*a* atoms substitute in the lattice for nearest neighbour pairs as schematically illustrated in Figure 1*d*. One atoms 16 of tin—a Group IV*a* element—has substituted for one atom of arsenic and one atom 17 of tin has substituted for an adjacent gallium atom. Thus, two atoms, each with four valence electrons, have been substituted for two atoms, one having three valence electrons and the other having five valence electrons, a total of eight valence electrons. Therefore, no holes or excess electrons are produced. This was apparently proven in the prior art by resistivity measurements on undoped gallium arsenide and tin-doped gallium arsenide. These measurements showed almost identical resistivities in the doped and undoped gallium arsenide. Prior resistivity measurements in III*a*-V*a* compounds doped with silicon and germanium also indicate nearest neighbour pair substitution and thus no action of these elements as donors or acceptors.

In applicant's experiments, however, it was discovered that P-type gallium arsenide, to which a tin dot had been alloyed, exhibited current rectifying characteristics indicating the presence of a PN junction produced by the conversion of a region of the gallium arsenide from P-type to N-type conductivity. From this, it was deduced that tin must enter the gallium arsenide crystals substituting for a gallium atom, as illustrated in Fig. 1*e*, to produce an excess electron 18. Silicon and germanium, which are also elements of Group IV*a*, act as donor impurities in III*a*-V*a* compounds, but not nearly so strongly as does tin. The explanation seems to be that both single atom and nearest neighbour pair substitutions occur when the

semiconductor compounds are doped with tin.

Although silicon, germanium and tin will all act as donors in gallium arsenide to some degree, tin is the preferred element for several reasons. First of all, tin has the lowest melting point of these three elements and, therefore, is more easily alloyd to the IIIa-Va compounds. Secondly, tin is more solid soluble in the gallium arsenide than are germanium and silicon. Thirdly, tin is a stronger donor impurity than the other two elements, probably because it enters the semiconductor substituting for nearest neighbour pairs only to a slight degree as compared with silicon and germanium.

The strong doping properties of tin in gallium arsenide make it an excellent material for use in forming the emiter of gallium arsenide transistors.

A gallium arsenide NPN diffused base transistor may be produced using the technique illustrated in Fig. 2*a*—*c*. A starting wafer 31 of N-type conductivity has diffused into its surface to a depth of a few mils a P-type conductivity impurity such as zinc to produce a P-type "skin" as shown by the dashed lines in Fig. 2*a*. The resulting P-type gallium arsenide is then removed from all but one surface of the wafer, as by etching, leaving only the P-type region 32 beneath the one surface. Tin is then evaporated onto a small region 33 of the P-type surface, and a zinc-gold alloy is evaporated onto another small region 34 adjacent the tin. The wafer is then heated to from about 600° C. to about 800° C. for a time sufficient to alloy the tin and the zinc-gold alloy to the wafer. The wafer is then masked in an area immediately surrounding the two alloyed contacts and the unmasked P-type region removed by etching to produce a "mesa" structure (see Fig. 2*c*) in the conventional way. After removal of the masking material, leads 35 and 36 are attached as by thermal compression bonding to the two alloyed regions, and a tab 37 is soldered to the N region of the wafer. The N-type region 31*a* of the wafer comprises the collector of the transistor and the P-type diffused region 32*a* of the mesa, the base. The zinc-gold alloy contact 34, forming an ohmic contact to the P-type region, acts as the base contact to the transistor and the tin-alloyed contact 33, forming a rectifying contact with the P-type region, acts as the emitter contact of the transistor.

A gallium arsenide NPN alloy transistor can be made by alloying tin into opposite sides of a P-type gallium arsenide wafer. Such a transistor (before the attachment of leads) is shown in Fig. 3 wherein the tin emitter dot is designated as 41 and the tin collector dot is designated as 42. Contact to the base region—bulk of the P-type gallium arsenide wafer 43—is achieved by an alloyed silver-zinc ring 44.

It is to be recognized that tin may be diffused, rather than alloyed, into gallium arsenide to produce N-type doping. For diffusion, the gallium arsenide wafer is sealed in an evacuated ampoule of quartz or similar material, together with a small amount of tin so arranged that the tin is not in contact with the wafer. The ampoule and its contents are then heated to from 800° C. to 1000° C. for a period of from one hour to about fifty hours.

The donor doping properties of tin which make this material useful in the formation of rectifying contacts to P-type gallium arsenide, also make this material excellent for the formation of ohmic contacts to N-type gallium arsenide.

The processes outlined above for the manufacture of various gallium arsenide transistors have been described omiting certain necessary etching, cleaning, and other steps, all of which are usual and conventional in the art in the production of transistors, since these particular steps form no part of the inventive concept of the present invention.

WHAT WE CLAIM IS:—

1. A transistor comprising a body of gallium arsenide having therein a region of P-type conductivity, and having alloyed to at least a portion of said region of P-type conductivity a body comprised of tin or principally of tin.

2. A transistor according to Claim 1, in which said region of P-type conductivity is diffused.

3. A transistor according to Claim 1 or 2, wherein there is included a body of zinc and gold alloyed to said region of P-type conductivity at a point spaced from the body comprised of tin.

4. A transistor according to Claim 1, including an additional body comprised of tin alloyed to said region of P-type conductivity at a point spaced from the first body of tin.

5. A transistor according to Claim 4, wherein there is included a silver-zinc ring alloyed to said region of P-type conductivity.

6. A gallium arsenide transistor substantially as herein described with reference to Figs. 2*a* to 2*c* of the accompanying drawing.

7. A gallium arsenide transistor substantially as herein described with reference to Fig. 3 of the accompanying drawing.

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