July 1, 1958 S. E. MAYER 2,841,510

METHOD OF PRODUCING P-N JUNCTIONS
IN SEMI-CONDUCTOR MATERIALS
Filed May 25, 1955

FIG. 1.

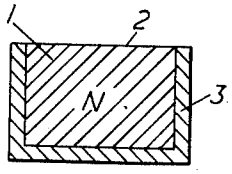


FIG. 2.

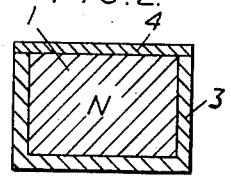


FIG. 3.

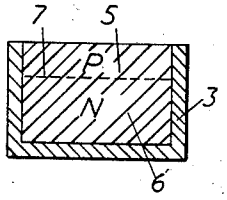


FIG. 4.

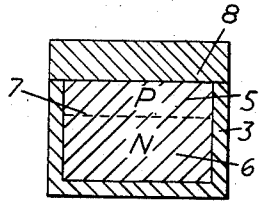


FIG. 5.

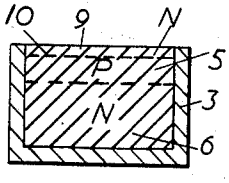
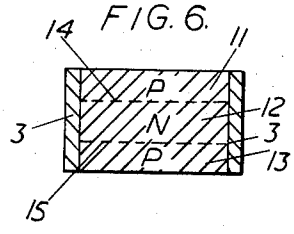


FIG. 6.



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METHOD OF PRODUCING P–N JUNCTIONS IN SEMI-CONDUCTOR MATERIALS

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6 Claims. (Cl. 148—1.5)

The present invention relates to the treatment and preparation of electric semi-conducting materials such as are used for electric rectifiers or crystal triodes, or energy detectors.

Hitherto, single crystals of certain elements such as silicon or germanium taken from group 4 of the periodic table of elements have been commonly used as semiconductor materials, but other semiconductors consisting of chemical compounds between certain elements from groups 3 and 5, such as aluminium antimonide, are now being investigated.

The electrical conductivity of semi-conductors such as germanium is generally considered to depend on the presence in the crystal of a certain number of lattice irregularities.

These can be two kinds:

(1) The kind in which a small percentage of the atoms of the crystal are replaced by some other element or elements; and

(2) The kind in which the crystal has lattice defects, that is, a percentage of the atoms are missing altogether from the lattice, or are displaced from their proper positions.

Lattice irregularities of type 1 may be produced by the addition to the basic semiconductor material (such as germanium or silicon) of a small percentage of a donor element, such as arsenic, from group 5 of the periodic table. In that case there are produced a small number of easily detached electrons which can act as current carriers, and the semi-conductor is then said to be of the N-type, or to have N-type conductivity. Type 1 irregularities may also be produced by the addition of a small percentage of an acceptor element, such as aluminum, from group 3 of the periodic table. In that case the crystal lattice is deficient in electrons and there are present a number of sites in the lattice where an electron is missing, which are called "holes," and which act like positive current carriers. The semiconductor is then said to be of the P-type, or to have P-type conductivity. It should be pointed out, also, that gold has been found to be a very effective acceptor element.

Type 2 lattice irregularities, namely lattice defects, have substantially the same effect as the addition of acceptor elements and produce P-type conductivity.

For convenience, the elements added, or present in small percentages, for controlling the conductivity type of the semiconductor, will be called "significant impurities," and will be referred to as donor or acceptor impurities according as the corresponding elements are donor or acceptor elements.

When lattice irregularities due to any or all of the above described causes are present, the resulting type of conductivity of the semiconductor is determined by the preponderating cause. For example, if both donor and acceptor impurities are present in a region of the semiconductor, the conductivity of that region will be

N-type or P-type according as the donor or the acceptor impurity atoms are in the majority.

In the manufacture of semi-conductor devices, it is often desired to produce a semi-conducting crystal with two or more regions of alternately P- and N-type conductivity separated from one another by what are called P–N junctions. One method of doing this is described in the specification of British Patent No. 753,133. Very briefly, it consists in starting with a slice from a semi-conducting crystal having N-type conductivity, depositing on one surface of the slice a thin film of an acceptor impurity, and then heating the crystal to a suitable temperature for diffusing the acceptor impurity into the crystal. If sufficient quantity of the acceptor impurity is used, a layer of the crystal will be converted to P-type conductivity, and a P–N junction will be formed at a depth below the surface depending on the heat treatment.

The difficulty which has been encountered with this method is that the heat treatment causes the significant impurity to spread very rapidly over all the surfaces of the crystal slice, so that a P-type layer is formed on every such surface, and has to be ground off where it is not wanted.

The object of the present invention is to prevent the unwanted spreading of the deposited significant impurity over the surface of the crystal. It is believed that this spreading is largely due to the existence at the surface of relatively large numbers of lattice defects of the kind in which atoms are missing from the lattice.

Accordingly, the invention provides a remedy which has been found to be effective in preventing this unwanted spreading. This remedy consists in depositing on the surface or surfaces of the semiconductor, which is or are not to be covered by the significant impurity, a film of an inhibiting element which is isomorphous with the basic semiconductor material but different therefrom (or a compound of such an element), at some stage before the heat treatment for diffusing the significant impurity into the semiconductor is applied. Stated more specifically, the inhibiting element is taken from group 4 of the periodic table in the case where the semiconducting crystal is silicon or germanium.

The invention also provides a semiconductor device employing a semiconductor which has been treated in the manner just stated.

In practice, the most convenient inhibiting element for a germanium crystal has been found to be silicon, either in the elementary form, or in the form of silicon monoxide.

One example of the process according to the invention will be explained with reference to the drawing accompanying the provisional specification, in which Figs. 1 to 6 show sectional views of a semiconducting crystal illustrating stages in the process.

In these figures the thickness of layers and films on the surface of the crystal is greatly exaggerated in order to show the details clearly.

Referring to Fig. 1, a slice of a germanium crystal 1, assumed to be of the N-type, and having a specific resistance of about 5 ohm-cm., for example, is shown in section. The crystal slice may be circular in plan, or rectangular, or of any other form. The slice, having been cut to the desired shape, is first etched with any suitable etching solution to remove impurities from the surface, and any disturbed material produced by the cutting operations, and is then washed and dried. It will be assumed that it is desired to produce a P–N junction at some convenient distance below the top surface 2. The next step according to the invention is to evaporate, or otherwise deposit in some suitable way, on all other surfaces of the slice, a thin film or coating of silicon

monoxide 3. This film may for example be 10^{-6} inch thick.

A film 4 (Fig. 2) of an acceptor impurity element, such as gold, for example, is then evaporated or otherwise deposited on the upper face of the crystal. This layer may be about 2×10^{-7} inch thick, for example, and the crystal is then heated at a temperature of about 850° C. for about 4 hours in order to diffuse the gold into the crystal.

The atoms of gold will convert the upper portion of the crystal to P-type conductivity, thereby producing a P-type region or layer about 0.008 inch thick, shown at 5 in Fig. 3. Between the layer 5 and the main portion 6 of the crystal there will be produced a P–N junction 7, shown as a dotted line, about 0.008 inch below the surface. As already explained, the film 3 prevents the gold from spreading over the whole surface of the crystal during the heat treatment.

If a second P–N junction is required, the process may be repeated. As shown in Fig. 4, the crystal with its P- and N-type regions 5 and 6 already formed has again deposited on its upper surface, by evaporation or otherwise, a thin film 8 of a suitable donor impurity element such as antimony. This film may for example, be about 10^{-4} inch thick. The crystal is again heated at a temperature of about 850° C. for about five minutes in order to diffuse the donor element into the P-type layer, thereby reconverting its upper portion to N-type conductivity. In this way an N-type layer 9 (Fig. 5) is formed, which may be 0.001 inch thick, for example. A second P–N junction 10 is thus formed, the crystal being divided into three regions with respectively N-, P-, and N-type properties. As before the spread of the donor impurity element over the whole surface of the crystal is prevented by the film 3.

It will be evident from Figs. 1, 2 and 3 that if the portion of the film 3 on the lower surface of the crystal 1 be omitted (the portions on the sides of the crystal still remaining, a gold film may be deposited on both the upper and lower surfaces. After diffusion for 4 hours at 850° C., a crystal as shown in Fig. 6, with three regions 11, 12, 13 having respectively P-, N-, and P-type conductivity will be produced, separated by P–N junctions 14, 15 about 0.008 inch from the upper and lower surfaces.

It will be evident also that a crystal with any number of regions with alternately P- and N-type conductivity may be produced by repeating the process described with reference to Figs. 1 to 5 using deposited films of alternately acceptor and donor elements on the upper surface of the crystal.

It should be mentioned that the heating necessary for the significant impurities generally produces lattice defects in sufficient number to convert the whole crystal to P-type conductivity irrespective of the presence of donor impurities. Therefore, in order to remove these unwanted lattice defects, the crystal should be annealed at a temperature of about 500° C. after heating for the diffusion of the significant impurities.

It will be understood that although in the above process gold is used as an acceptor element, various others, such as aluminium, gallium, or indium could be used. Likewise, for a donor element, phosphorus, arsenic or bismuth, for example, could be used instead of antimony.

While the preferred material for the film 3 is silicon monoxide, pure silicon could alternatively be used, or some other element from group 4 of the periodic table, which however, should be different from the material of which the crystal 1 consists.

It should be understood also that it is not essential that the basic semiconductor material should be germanium; silicon could be used, or one of the compound materials mentioned above. Further, the original crystal could be P-type instead of N-type, in which case a donor impurity element would be used for the film 4 in Fig. 2 instead of an acceptor element, and an acceptor element for the film 8 in Fig. 4 instead of a donor element; and the crystal produced would then be of the P–N–P type, like that shown in Fig. 6.

The thickness of the deposited films, and the time and temperature used for the diffusion process, which have been given above as examples, are not in any sense essential to the invention, and will be varied according to the conditions which have to be met.

It should be added that the inhibiting film 3 can be applied after depositing the film of the significant impurity on the surface of the crystal instead of before, but it must be present before any heating for diffusion of the impurity into the semiconductor. When several successive diffusion processes are applied, it will not generally be necessary to reapply the film 3 after each diffusion process.

It will be understood that a semiconductor having one or more P–N junctions produced in the manner explained above may be provided in any suitable way with electrodes to form a rectifier or crystal triode, or other semiconductor device.

While the principles of the invention have been described above in connection with specific embodiments, and particular modifications thereof, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the invention.

What I claim is:

1. A method of treating a body of semi-conductor crystalline material selected from the class consisting of germanium and silicon and of given conductivity type for the purpose of producing therein a P–N junction, comprising the steps of depositing on a given surface of the body a film of a significant impurity element of the kind adapted, when added to the semi-conductor material, to produce conductivity of the type opposite to the given type, and heating the body to a temperature sufficient to cause the significant impurity element to be diffused into the body, characterised in this, that at some stage before the body is heated, there is deposited on all other surfaces of the body except the given surface a film of a material selected from the class consisting of an element and an inorganic compound of such element taken from group IV of the periodic table which is isomorphous with the semi-conductor material, but different therefrom.

2. A method of treating a germanium crystal of given conductivity type for the purpose of producing a P–N junction below a given surface of the crystal, which comprises the steps of depositing on all surfaces of the crystal other than the given surface a film of a material selected from the class consisting of silicon and an inorganic compound of silicon, then depositing on the given surface a film of a first significant impurity element of the kind adapted, when added to germanium, to produce conductivity of the type opposite to the given type, and then heating the crystal to a temperature sufficient to cause the impurity element to be diffused into the crystal.

3. A method according to claim 2 which comprises the additional steps of depositing on the given surface a film of a second significant impurity element of the kind adapted, when added to germanium, to produce conductivity of the given type, and then heating the crystal to a temperature sufficient to cause the impurity element to be diffused into the crystal, for the purpose of producing a second P–N junction below the given surface.

4. A method of treating a germanium crystal slice of given conductivity type for the purpose of producing two P–N junctions between the two opposite faces of the slice, which comprises the steps of depositing on those surfaces of the crystal other than the said faces a film material selected from the class consisting of silicon, and an in-

organic compound of silicon, then depositing on each of the said faces a film of a first significant impurity element of the kind adapted, when added to germanium, to produce conductivity of the type opposite to the given type, and then heating the crystal to a temperature sufficient to cause the said first significant impurity element to be diffused into the crystal slice from each of the said faces.

5. A method according to claim 4 in which the said inorganic compound of silicon is silicon monoxide.

6. A method according to claim 4 in which the said crystal is of N-type conductivity, and in which the said first significant impurity element is gold, and in which the said second impurity element is antimony.

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