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METHOD OF ALLOYING AN ELECTRODE TO A GERMANIUM SEMI-CONDUCTIVE BODY

Johannes Jacobus Asuerus Ploos van Amstel, Eindhoven, Netherlands, assignor, by mesne assignments, to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware

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This invention relates to methods of manufacturing alloy electrodes on semi-conductive bodies of germanium. The term "alloy electrode" is to be understood in this case to mean an electrode obtained by providing on the body by melting or fusion a certain amount of a suitable element or a suitable alloy, followed by cooling. Such semi-conductive bodies having one or more alloy electrodes are frequently used in crystal diodes, transistors and other semi-conductive devices. It may be assumed that, during melting, part of the semi-conductive material dissolves in the melt and, during cooling, recrystallizes and grows on the original crystal lattice, but now with a certain content of the element or one of the elements from the melt. The material grown may thus have a conductivity-type which differs from that of the initial material. The element or the alloy is so chosen that the electrode acquires the desired electrical properties. In most cases, the electrode must be of the rectifying type, the element or the alloy then being required to have donor or acceptor properties depending upon whether the germanium is of the p-type or the n-type. In the first case, the alloy may consist of or contain antimony or arsenic; in the latter case, the alloy may consist of or contain indium, or gallium.

It has previously been suggested to utilize fusing agents for the manufacture of such alloy electrodes, but such agents or fluxes have the disadvantage that residues or disintegration products thereof lead to large leakage currents with rectifying electrodes.

The object of the invention is inter alia to provide a method of manufacturing such electrodes, in which said disadvantages do not occur.

According to the invention, the alloy electrode is first applied by fusion at a temperature below 450° C. and then subjected to afterheating at a temperature higher than the fusion temperature and at any rate higher than 350° C., the fusing agent or flux used during the first heating being a substance which may constitute the halide of the element or alloy applied by fusion and which has a vapour tension or pressure of at least 10 mms. mercury pressure at the temperature of the afterheating process.

When use is made of this method, fusing agents which may satisfactorily be used are the halogens themselves, the halogen-hydrogen acids, several halides having a high vapour tension and the halogen-hydrogen-molecule-complexes of organic compounds of the halides, in particular the halides of the donors or acceptors present in the electrodes can be used very well.

The invention will now be explained with reference to some examples for the manufacture of transistors.

Example I

A small ball of indium having a weight of 3.5 mgs. is laid on a thin disc of germanium of the n-conductivity type having a thickness of 150 microns. The whole is

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heated in a tube up to a temperature of 300° C. while passing dry hydrogen through the tube. Melting together then does not take place or substantially does not take place. Now, for several seconds, a little hydrochloric acid, as a flux, is added to the gas passed through, the quantity of which is not critical. Immediately thereafter, wetting occurs and the ball of indium and the germanium melt together. However, on account of the low temperature, the germanium substantially does not dissolve in the indium, and thus no penetration of the liquid-solid interface occurs. In a similar manner, a second small ball of indium having a weight of 0.8 mg. is secured by melting to the other side of the germanium disc. At the same time, a base contact is secured by soldering with the use of tin.

Subsequently, nitrogen with a trace of oxygen (which serves to prevent the flowing out of the indium) is passed through the tube and the temperature is increased to 600° C. for a few seconds or longer. The acid residue, for example traces of indium-chloride, evaporate completely during this, or the preceding treatment and are carried away completely by the flow of nitrogen, while the indium alloys further with the germanium and the alloy now penetrates the disc to form a junction at the desired depth.

The halogens themselves or other halogen-hydrogen acids may be used as a fusing agent, by applying them in gaseous form, the same as has been described in relation to hydrochloric-acid. If, however, the halogens would react violently with the hydrogen, it is preferred to use nitrogen as a carrier.

Many other metals and alloys may be fused on germanium in the same way as described here with regard to indium. So for instance lead containing 2-10 percent (by weight) of antimony, bismuth containing 2% of gallium, tin containing 52% of indium, tin containing 5-10% antimony or 1% arsenic, and lead containing 24% tin plus 1% antimony. Some of the electrodes made from these alloys are used only as ohmic contacts.

Example II

A small ball consisting of indium is moistened with a saturated solution of pyridine-hydrochloride in water. It is laid on a thin disc of germanium and heated in a tube to approximately 300° C. for 2-5 minutes while passing through dry hydrogen. The indium now readily flows out on the germanium while obtaining very good adhesion to define the ultimate alloying area, but no penetration of the alloy front occurs. In a similar manner, a second small ball of indium is provided by fusion on the other side, at the same time a base contact being secured by soldering with the use of tin. Finally, an afterheating treatment is carried out as in the first example to cause the desired extent of penetration of the alloy front.

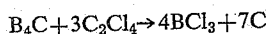
For moistening, use may also be made of other halogen-hydrogen-molecule-complexes of organic compounds, such as aniline-chlorohydrate, dimethylaniline-chlorohydrate and guanidine-chlorohydrate. Good results have also been obtained with solutions of indium chloride, indium bromide and indium iodide in water, notwithstanding the hydrolysis of such solutions.

Example III

Germanium pellets on which small balls of indium have been laid are heated in a tube at about 350° C. in a flow of a mixture of hydrogen and nitrogen. As soon as the indium has been molten, some nitrogen containing boron chloride is passed over the pellets causing good adherence of the indium to the germanium. The treatment of heating in the mixture of hydrogen and nitrogen

is then continued until the whole treatment has taken about five minutes. Afterheating is carried out as described in Example I.

The boron chloride may be prepared by reaction of dicarbontetrachloride on boron carbide according to



It will be evident that it is advantageous to utilize a fusing agent or flux having a vapour pressure which is as high as possible within practical limits. It is preferable to ensure that the electrode applied by fusion does not contain elements leaving residues which are difficult to evaporate with the fusing agent. If a residue should remain, it must at any rate be removed during the etching process which usually follows the fusion process.

What is claimed is:

1. A method of alloying an electrode to a germanium semi-conductive body, which comprises placing an electrode-forming material in engagement with said germanium body, preheating said body and electrode-forming material in the presence of a gaseous or liquid flux and at a first temperature below 450° C. and for a predetermined time interval at which the electrode-forming material fuses and adheres to but does not substantially penetrate the germanium body thereby to define the alloying area, thereafter reheating the body and material at a second temperature above 350° C. and above the first temperature and at which the said material substantially penetrates the germanium body to the required degree, said flux being constituted of a readily-volatilizable halogen-ion-donating material having a vapor pressure at said second temperature of at least 10 mms. of Hg and reacting with said body and material to produce only readily-volatilizable residues, whereby detrimental residues of said flux on the germanium body are avoided.

2. A method as set forth in claim 1 wherein the flux is a halide of an element of the electrode-forming material.

3. A method as set forth in claim 2 wherein the electrode-forming material is constituted principally of indium, and the flux is indium chloride.

4. A method as set forth in claim 1 wherein the flux is a halogen.

5. A method as set forth in claim 1 wherein the flux is a halogen-hydrogen-molecule-complex of an organic compound.

6. A method as set forth in claim 1 wherein the flux is a halide.

7. A method of making an alloy electrode to a germanium semiconductive body, comprising the steps of heating the body with electrode material in juxtaposed

relationship at a temperature below 450° C. in a substantially non-oxidizing atmosphere, adding to said atmosphere a small amount of hydrochloric acid as a flux to cause the electrode material and body to wet one another and fuse without any substantial penetration occurring, thereafter heating the body and material at a second higher temperature, above 350° C., to cause the required degree of penetration to occur.

8. A method of alloying an electrode to a germanium semiconductive body, which comprises placing an electrode-forming material in engagement with said germanium body, preheating said body and electrode-forming material in the presence of a liquid flux and at a first temperature below 450° C. and for a predetermined time interval at which the electrode-forming material fuses and adheres to but does not substantially penetrate the germanium body thereby to define the alloying area, thereafter reheating the body and material at a second temperature above 350° C. and above the first temperature and at which the said material substantially penetrates the germanium body to the required degree, said liquid flux being constituted of a readily-volatilizable halogen-hydrogen acid having a vapor pressure at said second temperature of at least 10 mms. of Hg and reacting with said body and material to produce only readily-volatilizable residues, whereby detrimental residues of said flux on the germanium body are avoided.

9. A method of alloying an electrode to a germanium semi-conductive body, which comprises placing an electrode-forming material in engagement with said germanium body, preheating said body and electrode-forming material in the presence of a flux consisting essentially of hydrochloric acid and at a first temperature below 450° C. and for a predetermined time interval at which the electrode-forming material fuses and adheres to but does not substantially penetrate the germanium body thereby to define the alloying area, thereafter reheating the body and material at a second temperature above 350° C. and above the first temperature and at which the said material substantially penetrates the germanium body to the required degree, said flux reacting with said body and material to produce only readily-volatilizable residues, whereby detrimental residues of said flux on the germanium body are avoided.

References Cited in the file of this patent

UNITED STATES PATENTS

2,761,800	Ditrick	Sept. 4, 1956
2,807,561	Nelson	Sept. 24, 1957