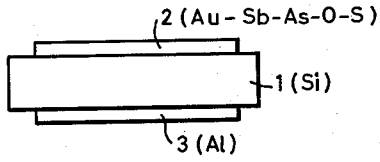
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METHOD OF PRODUCING A SILICON SEMICONDUCTOR DEVICE

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METHOD OF PRODUCING A SILICON SEMICONDUCTOR DEVICE

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9 Claims. (Cl. 148—1.5)

Our invention relates to electric semiconductor devices such as rectifiers, power transistors or photodiodes, whose semiconductor body consists of substantially monocrystalline silicon, and is an improvement over the method disclosed and claimed in the copending application of Norbert Schink and Adolf Herlet, Serial No. 711,967, filed January 29, 1958, now U.S. Patent No. 2,959,501, assigned to the assignee of the present invention. More specifically, therefore, our invention concerns the manufacture of semiconductor devices in which the silicon crystal is fusion-joined with a contact electrode consisting of a gold-antimony alloy with 0.2 to 5%, preferably about 1%, antimony and a trace content of arsenic, the amount of arsenic being between 0.001 and 0.1% relating to the total quantity of the gold-antimony alloy. It is an object of our invention to further improve the reliability and uniformity of the silicon semiconductor devices made with the aid of a process of the type mentioned above.

In accordance with our invention we provide the gold-antimony-arsenic alloy with an additional trace content of oxidic oxygen before alloying the alloy together with, and into the adjacent surface zone of the silicon monocrystal. By "oxidic oxygen" we mean oxygen present or available as the oxide.

We have found that particularly favorable results with respect to the absence of faults in the products are obtained if the oxygen addition is between 0.01% and nearly 0.1% relating to the total weight of the gold-antimony-arsenic alloy.

For adding the oxygen, the quantity of antimony or a portion thereof, to be used for forming the alloy, is first roasted in pulverulent form within an oxygen-containing atmosphere, for example in air. Another method is to first admix the arsenic to the antimony, and then to roast the quantity of antimony, or a portion thereof, required for forming the alloy, in pulverulent form within an oxygen-containing atmosphere, for example air. A further way of adding the oxygen is to produce an alloy of arsenic-containing antimony and oxygen-containing antimony and then alloying this alloy together with the pure gold in the proper proportions. For this purpose the gold content can be incrementally increased during several successive melting processes whereby an accurate dosage is more readily obtained.

According to the copending application of Adolf Herlet, Hubert Patalong and Norbert Schink, Serial No. 769,295, filed October 24, 1958, now U.S. Patent No. 2,937,113 and assigned to the assignee of the present invention, the gold-antimony alloy to be alloyed into the silicon monocrystal may be provided with a trace content of sulfur, preferably between 0.0001% and 0.1% relating to the total weight of the gold-antimony alloy. Such a trace content of sulfur can also be additionally provided in the method according to the present invention. For this purpose, for example, a pre-alloy can be prepared from different kinds of antimony, namely of

arsenic-containing antimony, oxygen-containing antimony, and sulfur-containing antimony. This pre-alloy is then alloyed together with pure gold preferably in a stepwise manner as described above.

An embodiment of producing an alloy according to the invention will be described presently. The process is carried out by first preparing three different kinds of antimony, A, B and C.

Antimony A

95 grams antimony are melted together with 5 grams arsenic at approximately 610° C.

Antimony B

100 grams antimony powder are roasted in air at a gradually increasing temperature and are thus heated up to melting temperature of approximately 635° C. After cooling the oxygen-containing antimony, the oxygen content is determined by analysis. On the average, an oxygen content of 2% will be determined. However, departures from this value may occur, for example due to differences in the granulation of the antimony powder, differences in the duration or program of the heating process, or differences in the amount of the maximum temperature being reached.

Antimony C

100 grams antimony powder are melted together with 2 grams flowers of sulfur by heating at about 635° C. The sulfur content is determined by analysis. It is assumed, for example, that a sulfur content of 1% is thus found. However, departures from this value may also occur as a result of the differences in the performance of the melting process mentioned in the foregoing paragraph.

For obtaining the correct proportion of the various additions to be made to the gold-antimony alloy ready for use, suitable quantities of the antimony kinds, A, B and C are melted together with an additional quantity of pure antimony at a temperature of approximately 635° C. By calculation, the following weight proportions are determined for the example dealt with above:

$$2A+50B+10C+38\ Sb$$

In this manner, there is obtained an antimony-arsenic-oxygen-sulfur alloy with 0.1% arsenic, 1% oxygen and 0.1% sulfur. A portion of this pre-alloy, for example 100 grams, are melted together with 300 grams pure gold at about 360° C. This mixing proportion corresponds to the Au/Sb eutectic with a content of 25% Sb. When 400 grams of this eutectic alloy are melted together with 9600 grams pure gold at about 1100° C., the resulting composition in the amount of 10 kilogram consists of ready-for-use gold-antimony alloy with the desired trace contents of added elements. The necessary quantities required for alloying the metal into the silicon monocrystals can then be taken from this supply. For this purpose it is preferable to roll the above-mentioned gold-antimony alloy into the form of foils. This can be done without particular difficulty with an alloy containing the above-stated quantities of individual alloy components.

For the production of rectifiers it had been found advantageous to roll the foil thickness down to about 0.1 mm. For the production of transistors, foils rolled down to a thickness of about 0.04 mm. have been found to be favorable.

It is preferable to perform the above-described melting processes in an atmosphere of inert gas, for example argon, nitrogen or carbon monoxide, because otherwise the desired dosage of the respective additions, under certain circumstances, may be affected by uncontrolled evaporation. Such danger is particularly present when using temperatures above 500° C., and also in melting processes

in which the antimony content of the melt is very small in comparison with the eutectic Sb/Au ratio of 25%.

Tests have shown that, in conjunction with the above-described trace additions of oxygen and/or sulfur, the arsenic content can be reduced down to one order of magnitude smaller than stated in the example, namely down to 0.0001% of the total quantity of the gold-antimony alloy, without appreciably decreasing the desired result.

The method of joining of the electrode with the silicon body by the formation of a diffusion alloy at the boundary zone is described in detail in our copending application Serial No. 711,967. One such method is effected by assembling disc-shaped silicon bodies on both sides with electrode foils located in face-to-face area contact therewith. Any desired carrier plates may also be assembled by placing them onto the foil electrodes. The entire assembly is then placed between pressure plates, for instance of graphite, and is clamped between these plates while being heated to a temperature between about 700° and 800° C. for approximately 5 to 10 minutes. This suffices to produce the desired alloyed fusion joint between the silicon body and the electrode foil according to the invention. Another method of joining the electrode with the silicon body is described in the copending application of R. Emies, Serial No. 637,029, filed January 29, 1957, and assigned to the assignee of the present invention.

Illustrated on the drawing, by way of example, is a silicon rectifier made according to the present invention.

The rectifier comprises a monocrystalline semi-conductor body 1 of p-conducting silicon, shaped as a flat cylinder of approximately 0.4 mm. thickness and a diameter of approximately 10 mm. Joined with the top surface of the silicon crystal is an electrode 2 of gold foil containing approximately 99% gold, approximately 1% antimony, a trace of arsenic amounting to about 0.01%, a trace of oxidic oxygen amounting up to about 0.01%, and may also contain a trace of sulfur amounting up to about 0.1%. The foil 2 has a thickness of about 0.05 mm. and a diameter of approximately 9 mm. Joined with the bottom surface of the silicon body 1 is an electrode 3 of aluminum having a foil thickness of approximately 0.05 mm. and a diameter of approximately 9 mm. Both electrodes are fushion-joined with the silicon body by one of the methods described above, so that an alloyed merger zone exists between each electrode and the semiconductor body, the alloy penetrating and diffusing somewhat into the silicon body. A barrier layer is formed in the boundary zone between the gold-alloy electrode 2 and the silicon body 1 so that the device has a symmetrical conductance.

A gold-antimony-arsenic-oxygen alloy according to the invention may also be used for producing a barrier-free junction. In this case, the silicon body must have n-type conductance. It will also be understood that various other metals, forming barrier-free contacts may be used as counter-electrode instead of aluminum foil 3.

It will be obvious to those skilled in the art, upon a study of this disclosure, that this invention permits of various modifications and alterations with respect to the individual method steps disclosed, and hence can be embodied in equipment other than as particularly illustrated and described herein, without departing from the essential features of the invention and within the spirit and scope of the claims annexed hereto.

We claim:

1. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and traces of arsenic and oxygen in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing a trace of oxidic oxygen in an amount between 10^{-2} to about 10^{-1}%, the remainder being substantially all gold; and alloying the composition together with the silicon body to form an area fusion joint between said body and said electrode.

2. The method according to claim 1, including the step of roasting antimony in pulverulent form within an oxygen-containing atmosphere at a temperature of approximately 635° C. to introduce said oxidic oxygen content.

3. The method according to claim 1, including the step of roasting arsenic-containing antimony in pulverulent form within an oxygen-containing atmosphere at a temperature of approximately 635° C. to introduce said oxidic oxygen content.

4. The method according to claim 1, including the steps of first forming a pre-alloy from arsenic-containing antimony and oxygen-containing antimony and thereafter alloying said pre-alloy with substantially pure gold.

5. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and traces of arsenic and oxygen in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing a trace of oxidic oxygen in an amount between 10^{-2} to about 10^{-1}%, the remainder being substantially all gold, and including the steps of first forming a pre-alloy from arsenic-containing antimony and oxygen-containing antimony and thereafter alloying said pre-alloy with substantially pure gold, stepwise increasing the quantity of said gold by adding portions of gold in a plurality of melting processes.

6. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and traces of arsenic and oxygen in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing a trace of oxidic oxygen in an amount between 10^{-2} to about 10^{-1}%, the remainder being substantially all gold; and alloying the composition together with the silicon body to form an area fusion joint between said body and said electrode, and including the step of providing said oxygen-containing gold-antimony-arsenic alloy with a trace content of sulfur in an amount between 10^{-4} and 10^{-1}% prior to alloying said composition together with the silicon body.

7. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and traces of arsenic and oxygen in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing a trace of oxidic oxygen in an amount between 10^{-2} to about 10^{-1}%, the remainder being substantially all gold, and including the steps of first forming a pre-alloy from arsenic-containing antimony, oxygen-containing antimony ad sulfur-containing antimony, and thereafter alloying said pre-alloy with substantially pure gold, stepwise increasing the quantity of said gold by adding portions of gold in a plurality of melting processes.

8. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and traces of arsenic and oxygen in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing a trace of oxidic oxygen in an amount between 10^{-2} to about 10^{-1}%, the remainder being substantially all gold, and including the steps of first forming a pre-alloy from arsenic-containing antimony by melting approximately 95% antimony with about 5% arsenic in an inert atmosphere at approximately 610° C. to form an antimony-arsenic alloy, roasting a quantity of powder containing a major amount of antimony in an oxidizing atmosphere at a temperature of approximately 635° C. to form an oxygen-containing antimony material, melting

a further quantity of antimony together with sulfur to form a sulfur-containing antimony material, combining approximately two parts by weight of said antimony-arsenic alloy, approximately 50 parts by weight of said oxygen-containing antimony material, approximately 10 parts by weight of said sulfur-containing antimony, and approximately 38 parts by weight of pure antimony by melting said proportionate parts in an inert atmosphere at a temperature of approximately 635° C. to form said pre-alloy, melting a portion of said pre-alloy with pure gold at a temperature of approximately 360° C. to form a gold-antimony eutectic alloy, subsequently melting said eutectic alloy in an inert atmosphere with a further quantity of pure gold at a temperature of approximately 1100° C., to form a further gold-antimony alloy, rolling said last mentioned alloy down to foil thickness; and alloying said foil together with the silicon body to form an area fusion joint between said body and said electrode.

9. The method of producing an electric semi-conductor device having a substantially monocrystalline silicon body and an electrode on said body, which comprises forming an alloyed composition of gold, antimony and a trace of arsenic in amounts between about 0.2 and 5% antimony and about 10^{-4} to about 10^{-1}% arsenic, and containing between 10^{-2} and 10^{-1}% of an element selected from the group containing oxygen and sulfur, the remainder being substantially all gold; and alloying the composition together with the silicon body to form an area fusion joint between said body and said electrode.

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